THE IGNITION CHARACTERISTICS
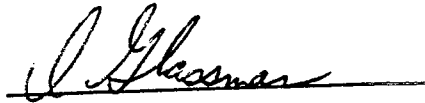
OF METALS

IN OXYGEN ATMOSPHERES

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ABSTRACT

The inefficient ignition of metal particles used as
an additive to solid propellants is one of the basic causes
for the failure of such fuels to meet theoretical perfor-
mance levels. In order to solve this particular problem, it
is of interest to study in detail the fundamental processes
governing the ignition of metal particles. Consequently, a
physical model of this heterogeneous process has been under
development at Princeton in the last few years. In this
report, this model is further refined and clarified so that
it can more easily explain some of the more interesting prop-
erties of metal ignition: (1) The ability of the metal to
self-heat to ignition above a certain "critical temperature".
(2) The importance of low temperature metal oxidation and the
ability of the consequent solid oxide coat to protect the
metal below a defined "transition temperature". (3) The so-
called pyrophoric behavior of metal particles.

Experimental results on the ignition of the more common
metals in an oxygen atmosphere form the main contribution of
the present report. This work was accomplished by means of
an induction furnace facility that allowed continuous moni-
toring of the metal sample temperature. The present compi-
lation of metal ignition temperatures will hopefully provide
the fundamental experimental data from which a more quanti-
tative model of heterogeneous metal ignition may be developed.

In addition, this report includes a discussion of cer-
tain experimental results which lead to the following impor-
tant conclusions: (1) The ignition temperature of a metal
may be controlled by the boiling point of that metal. (2)
The ignition temperature of a metal in the bulk configuration
is relatively consistent in an oxygen atmosphere.   (3) The

total ambient oxidizer pressure and the type of configuration
(surface or vapor-phase) in which a metal burns may also have
a significant effect on the ignition process.

ACKNOWLEDGMENTS

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CHAPTER I: INTRODUCTION

In the past decade, some of the more significant improvements in the area of chemical propulsion have come about through the use of metal additives in both solid and hybrid rocket systems. Specifically, an increase in performance is achieved which is primarily due to the characteristically large heat of reaction per unit mass associated with the combustion of certain light metals such as lithium, beryllium, aluminum, and magnesium.

Unfortunately, theoretical performance levels have not as yet been attained. Analyzing only the source of the chemical energy in these systems, it has been found that some losses can be due either to inefficient ignition or to inefficient combustion of the metal particles used as an additive to the fuel.

Although the combustion and the ignition processes are very closely related, it is usually worthwhile to attempt a separate study of these phenomena. To this end, Glassman, in 1959, suggested three principles that might govern the combustion for any metal sample (1,2)[1]:

(1) The boiling point of a metal oxide limits the flame temperature of the parent metal.

(2) If the boiling point of the metal oxide is greater than that of the parent metal, then combustion occurs in the vapor phase; if, on the other hand, the boiling point of the metal oxide is less than that of the parent metal, then combustion occurs on the metal surface.

(3) Radiation may be expected to play an important role in metal combustion.

The first principle is based on the observation that in general the heat of vaporization or dissociation of the metal oxide is greater than the heat generated in the appropriate metal-oxygen reaction. The second principle is a logical extension of the first. Since, for a vapor-phase diffusion flame,

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[1] Numbers in parantheses refer to references listed at the end of this report.

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it is necessary to have heat transfer from the reaction zone
to the metal particle, then the temperature characterizing
the reaction zone, i.e., the flame temperature, must be
larger than the surface temperature of the metal particle.
Now the surface temperature of the particle is limited to
the metal boiling point. Thus, in order to have steady state
vapor-phase combustion, it is necessary that the boiling point
of the metal oxide be greater than the boiling point of the
metal, and vice-versa for a surface combustion process. How-
ever, this is not a _sufficient_ condition for vapor-phase com-
bustion since extreme losses from the reaction zone in some
circumstances could lower the flame temperature below the
boiling point of the metal and thus lead to a surface combustion
configuration(3).

The third principle is simply an extrapolation from the
fact that in a metal diffusion flame(vs. a hydrocarbon flame),
there is a high number of radiating metal oxide particles
formed at high temperatures in the hot flame zone during the
reaction.

In addition to these three statements which are concerned
with the metal combustion process, Glassman also put forth
another statement dealing with the metal ignition process.
Noting that this ignition process may be a transition from a
surface oxidation reaction to a vapor-phase combustion re-
action, he indicated that the ignition phenomena could be en-
tirely different from the steady state combustion phenomena.
However, since the process of ignition had not as yet been
fully investigated, it was impossible to make at that time any
postulate regarding the extent of the correlation between the
phenomena of ignition and combustion.

On the other hand, the combustion of metals has received
wide investigation in the past decade. The results of many
experiments in this field have indicated that all three of the
above principles as postulated by Glassman are applicable in
the determination of the physical and chemical structure of the

metal flame. The reader interested in the metal combustion literature may wish to consult several survey articles in the field (4,5,6). More recent work is available in Ref. 7 and 8.

The impetus for a separate program to undertake a study of the ignition phenomena in metals at Princeton came about through certain results obtained in earlier work on combustion which made use of the ohmic heating of wire samples (4,9,10,11). Only those experiments with aluminum wires which have been anodized will be considered in the present discussion.[2] Such wires were generally used in order that ohmic heating could continue above the melting point of the metal.

While investigating the flames produced by aluminum wires, Brzustowski (4,9) found that the ignition temperature of aluminum in oxygen-argon atmospheres was very close to the melting point of aluminum oxide at pressures greater than 300 torr. In addition, Friedman and Macek (13) had shown that the Al_2O_3 coating must melt in order that aluminum undergo vapor-phase combustion. Recent work by Kuehl (14) has again shown that in general the ignition temperature of aluminum is very close to 2042°C., the melting point of the metal oxide.

Later, Mellor (10,11) carried out similar experiments with anodized aluminum wires in carbon dioxide-oxygen atmospheres. He observed two things that were very different from the results of Brzustowski. First, in the carbon dioxide-argon mixtures at pressures below 300 torr, a cylindrical vapor-phase diffusion flame appeared before the wire broke. Such a flame is shown in Fig. 1, which is reproduced from Ref. 11. On the other hand, in the oxygen-argon mixtures, the wire broke thereby exposing molten aluminum to the oxidizing atmosphere before a vapor-phase flame appeared (4,9). Secondly, on the basis of total power required at ignition, it was easier to ignite anodized aluminum wires at similar pressures in CO_2-Ar atmospheres than it was to ignite them in O_2-Ar atmospheres (10,11).

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[2]For a more general discussion see chapters I and II of Ref. 12.

FIGURE 1
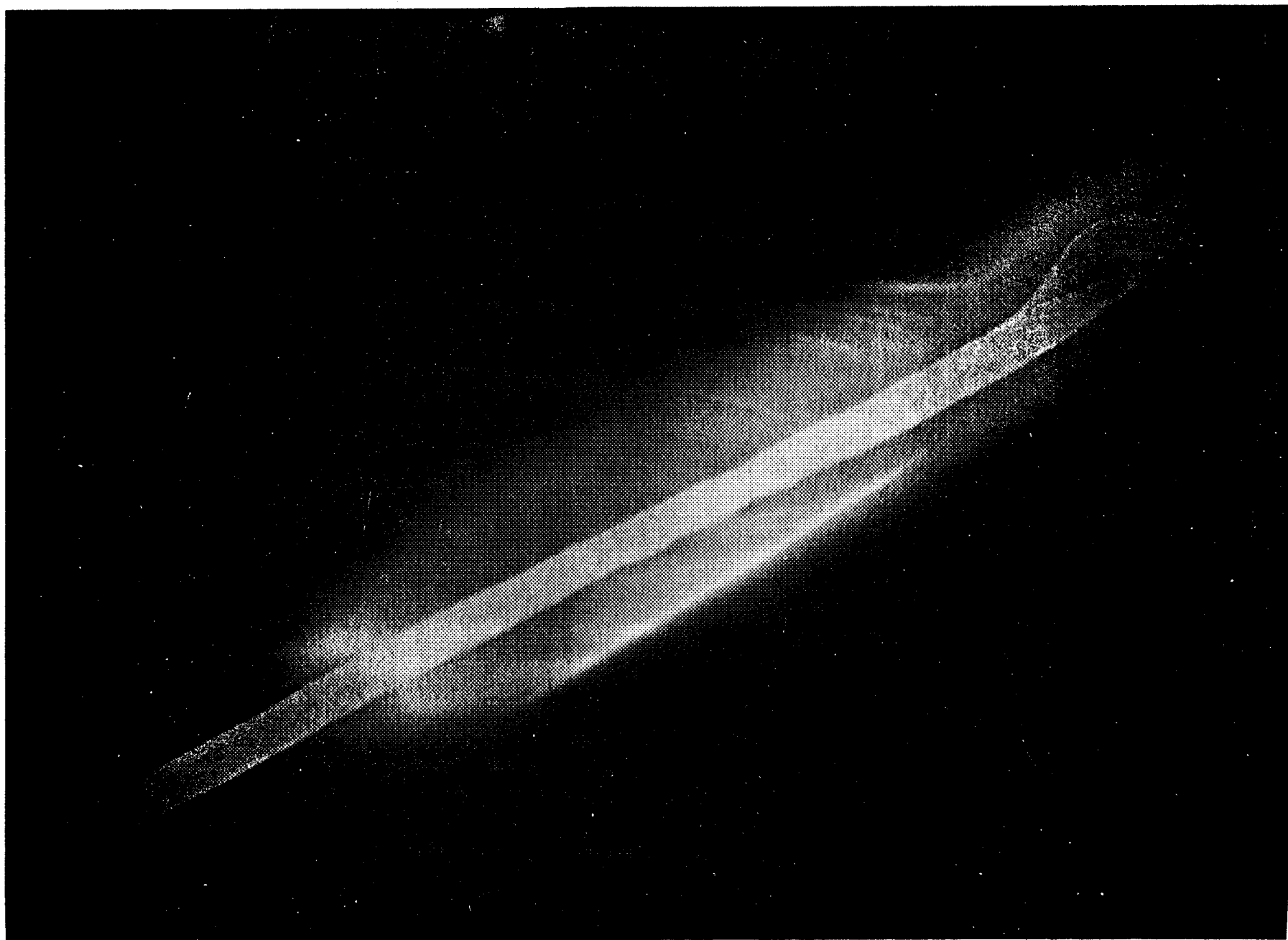
These results can be explained as follows: It is necessary here to consider the pre-ignition oxidation of the metal. In CO_2-Ar mixtures, little oxidation occurs during the pre-ignition period while in O_2-Ar mixtures, a very thick oxide coating builds up on the surface of the metal. In general, the anodized film is porous but in oxygen containing atmospheres, these pores are filled by the natural oxidation process during this pre-ignition period (15). Thus, in this case, melting of the oxide occurs before ignition can take place.

For an anodized film of Al_2O_3 considered here, a thin barrier layer of oxide exists between the outer porous layer and the metal substrate. Even in the case of a CO_2-Ar atmosphere however, it is suggested that the ignition temperature is still equal to the melting point of Al_2O_3 since only the barrier layer need be melted to expose the molten aluminum to this oxidizing atmosphere (15). Thus, in summary, since little oxidation occurs before ignition in a CO_2-Ar atmosphere and since the anodized coating is porous, ignition occurs in a cylindrical vapor-phase flame upon melting of the barrier layer before the wire breaks at that point when the anodized coating completely melts.[3] Obviously, because of the little oxide built up before ignition, the total power at ignition for the anodized wire is less in the CO_2-Ar mixtures than in the O_2-Ar mixtures.

This work with aluminum and other work with magnesium ribbons (4,9,10,11) showed primarily that the ignition of metals is strongly dependent on the pre-ignition surface oxidation reaction in the environment of interest. Surface oxidation reactions determine whether or not a particular metal coating is protective in a certain environment in a particular temperature range. If the metal coating is protective, then the metal sample cannot ignite. However, usually the oxide coating becomes nonprotective at higher temperatures and the sample may then ignite.

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[3] There appears to now be a more appropriate explanation for the appearance of this cylindrical vapor-phase flame which is discussed in detail in Chapter IV.

This surface coating is the unique property of the metal ignition problem that makes it very difficult to analyze mathematically. The ignition problem has been well treated for the homogeneous case, but is not al all well understood in the case of a simple heterogeneous reaction. Here the situation becomes even more difficult since we must consider the complicating factor brought about by the low temperature oxidation process common to all metals of interest.

These findings coupled with the well-known concepts of the homogeneous problem let to Mellor's work on the develcp- ment of both a model for the heterogeneous ignition of metals and subsequent experimental verification of certain trends predicted by that model (15,12). The present investigation seeks to further substantiate and clarify some aspects of the model primarily through an experimental determination of the ignition temperatures of many common non-toxic metals in an oxygen atmosphere. In addition to defining a bulk ignition temperature for these metals, the experimental results also lead to some other interesting conclusions which are dis- cussed in detail in Chapter IV.

Chapter III will be of much interest to the experimen- talist in the field since it attempts to go into great de- tail in describing some of the peculiar experimental diffi- culties in this type of work. It is believed that there is some experimental information here that is not well docu- mented in the literature.

The next chapter introduces the reader to the subject with a fairly thorough discussion of the steady state model of heterogeneous metal ignition as postulated by Mellor. Several changes have been made both in the presentation and interpretation of some aspects of this model. These have been integrated into the discussion and will be made clear at the appropriate time in only a few cases. The model as presented here, however, remains essentially that of Mellor.

The chapter closes with a discussion of the experimental information needed both to substantiate the model and to provide data needed to extend some of the concepts introduced by the model.

CHAPTER II: THE STEADY STATE MODEL OF METAL IGNITION

As mentioned previously, any model which attempts to describe the metal ignition process must take into consideration the formation of solid phase products on the surface during the pre-ignition reaction. Thus metal ignition is usually much more complicated than the heterogeneous ignition of other simple fuel-oxidizer systems. Because of this difficulty, Mellor developed a qualitative model of metal ignition based to a large extend on the classical thermal theories of homogeneous ignition as demonstrated most lucidly by Frank-Kamenetskii in his comprehensive work describing the effects of heat and mass transfer in chemical kinetics (16).

As is well known, both a stationary and a non-stationary approach exist for the description of the homogeneous ignition phenomena. Because of the complications involved in any heterogeneous process, it is best to emphasize the stationary approch in this case. It may be shown that the non-stationary approach can equally well describe the metal ignition process, but the argument is somewhat laborious (See Ref. 12). Therefore, since it is of interest here to only describe those aspects of the model directly essential to this particular work, the steady-state approach will be followed in order to make the principal ideas as clear as possible to the reader. Those interested in a detailed description of both the stationary and non-stationary aspects of the model along with an excellent discussion of the relationship between the classical thermal theories of homogeneous ignition and the present model may wish to consult Chapter II of Ref. 12.

It seems important at this time to indicate the limitations of Mellor's work. He attempted to construct a qualitative model which would take into consideration metals of all types and sizes in all possible atmospheres. An investigation of other models of metal ignition (12, 17) indicate that they are much more quantitative than the present description in that they

attempt to calculate ignition temperatures; however, each
of these models is restricted to only a very limited range
of practical experimental situations. Thus, although the
present description is admittedly very global and unfortunate-
ly cannot consider some of the important underlying chemical
phenomena involved in the actual ignition process, the con-
tribution of this model cannot be taken too lightly: It not
only brings together several concepts which have heretofore
not been well related in the literature, but more important-
ly, it attempts to elucidate those aspects of metal ignition
that are common to all possible cases involving this parti-
cular physical process. In so doing, certain criterion are
set up that must be met in order to have ignition for all
metals of all types and sizes in all possible atmospheres.

1. Heterogeneous Ignition with Gas-Phase Reaction Products

Before metal ignition, i.e., heterogeneous ignition with
solid-phase reaction products is considered, it is of para-
mount importance that a slightly simpler case be investigated,
that is, the ignition of a solid fuel via reaction with a
gaseous oxidizer involving only gaseous reaction products.
An example of this might perhaps be a carbon particle reacting
in air or oxygen (12).

As pointed out by Mellor (12), in the case of a heter-
ogeneous system, where the exothermic reaction occurs on the
surface as opposed to throughout a reaction volume as in a
homogeneous system, the interaction is characterized by a
uniform surface temperature T_s instead of a gas temperature,
and all heating terms are expressed per unit area instead of
per unit volume. Thus, in order to investigate the case of
a spherical metal particle in a static gaseous atmosphere for
which all the products are assumed to be in the gaseous state,
a heat balance is conveniently made in a thin control volume
at uniform surface temperature T_s enclosing only the reacting
surface of the metal.[1]

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[1]Since a steady-state system is being considered here, it is
necessary that the control surface be stationary. Therefore,
in this development, reactant depletion is neglected.

This heat balance is constructed by examining the rate of heat input and the rate of heat loss from the aforementioned thin control volume, both quantities being functions of the surface temperature T_s. Consider[2] first then the chemical energy release rate in cal/cm^2-sec. It may be written as:

$$\dot{q}_{chem} = \dot{m} Q \tag{II-1}$$

where $\dot{m}$ is the molar reaction rate in moles of fuel per cm^2 per second and Q is the chemical energy release in calories per mole of fuel.

The chemical energy release is given by the expression:

$$Q = \sum_{\substack{reactants \\ i}} n_i \Delta H_{i,T_s} - \sum_{\substack{products \\ j}} n_j \Delta H_{j,T_s} \tag{II-2}$$

where the subscript i indicates reactants and the subscript j products, where

$$\Delta H_{k,T_s} = \Delta H_{f,k}^{298} + \left(H_{T_s} - H_{298} \right)_k , \tag{II-3}$$

and where

T_s = surface temperature, $^\circ K$;

n_k = no. of moles of species k per mole of fuel;

$\Delta H_{f,k}^{298}$ = standard heat of formation of species k at 298$^\circ K$, cal/mole of k;

$H_{T,k}$ = enthalpy of species k at T$^\circ K$, cal/mole of k.

The molar reaction rate is given by two expressions, depending on whether the surface temperature T_s is such that the reaction rate is controlled by kinetics or by diffusion of the oxidizer. At lower temperature, $\dot{m}$ may be given by:

$$\dot{m} = A e^{-E/RT_s} C_s^n \tag{II-4}$$

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[2] In the present discussion, only <u>chemical</u> heat input will be considered.

where

A = pre-exponential factor, $cm^{3n-2}/moles^{n-1} \cdot sec$;

E = activation energy, cal/mole;

R = universal gas constant, $cal/mole \cdot °K$;

C_s = oxidizer concentration at the surface, mole of fuel/cm^3;

n = order of the reaction, dimensionless,

and therefore here the dependence of $\dot{q}_{chem}$ on T_s is exponential due to the controlling kinetic Arrhenius factor.

At higher temperatures, $\dot{m}$ may be given by:

$$\dot{m} = \frac{Nu\ D}{r}\left(C - C_s\right) \qquad (II-5)$$

where

Nu = diffusion Nusselt number, dimensionless;

D = diffusivity of the oxidizer, cm^2/sec;

r = a characteristic dimension of the system, cm;

C = oxidizer concentration of the gas, moles of fuel/cm^3;

and therefore here the dependence of $\dot{q}_{chem}$ on T_s is given predominantly by the diffusivity D which varies as the 1.67 power of temperature (18).

Thus as T_s is increased, the value of $\dot{q}_{chem}$ also increases due to the variation of Q with T_s, but the form of $\dot{q}_{chem}$ vs T_s is given by an S-shaped curve (See Fig. 2a) which emphasizes the control of the chemical heat release by the molar reaction rate, $\dot{m}$. At lower temperatures $\dot{m}$ is controlled by kinetics, but as T_s is increased, diffusion of the oxidizer through the inert gas to the particle surface becomes important and therefore $\dot{m}$ then is controlled by the diffusion process. In addition to diffusion, the drop in the slope of the $\dot{q}_{chem}$ vs T_s curve at higher temperatures is partially due to a small amount of dissociation of the reaction products.

Consider next the heat loss rate in $cal/cm^2 \cdot sec$ from the same control volume described previously. Recalling that this

control volume includes only the reaction surface, then the rate of heat loss $\dot{q}_{loss}$ may be written as follows:

$$\dot{q}_{loss} = \dot{q}_{cond,f} + \dot{q}_{cond,g} + \dot{q}_r \qquad \text{(II-6)}$$

where

$\dot{q}_{cond,f}$ = conductive heat loss into the fuel particle, $cal/cm^2 \cdot sec$;

$\dot{q}_{cond,g}$ = conductive heat loss into the ambient static gas, $cal/cm^2 \cdot sec$;

$\dot{q}_r$ = radiative heat loss to the environment, $cal/cm^2 \cdot sec$,

and where each of these terms is of course a function of the surface temperature T_s.

Notice that in this equation, there is no term indicating heat loss by means of mass transfer of gaseous products to the environment. In this analysis, the gas phase products are considered to be instantaaeously removed as they are produced at temperature T_s and they are not allowed to participate in any heat transfer to the environment. This approach is taken not solely for simplicity, but in looking forward to the adaptation of this model to the case of heterogeneous metal ignition as characterized by the deposition of a solid-phase product on the surface, it is recognized that such a product cannot participate in the transport of heat from the reacting surface to the environment.

By expressing each of the above terms explicitly, Eq. (II-6) can then be written in the following manner:

$$\dot{q}_{loss} = k_f \left.\frac{\partial T}{\partial r}\right|_{r=r_o^-} + k_g \left.\frac{\partial T}{\partial r}\right|_{r=r_o^+} + \epsilon\sigma\left(T_s^4 - T_r^4\right) \qquad \text{(II-7)}$$

where

k = thermal conductivity of the fuel or oxidizer gas (denoted respectively by subscript f or g), $cal/cm \cdot sec \cdot K$;

$\dot{q}_{chem}$ VS T_s

T_s

$T_s = T_{amb}$

$\dot{q}_{chem}$

c) $\dot{q}_{loss}$ VS T_s

T_s

$T_s = T_{amb}$

$\dot{q}_{loss}$

c) $\dot{q}_{chem}$ AND $\dot{q}_{loss}$ VS T_s

T_s

$\dot{q}_{loss}$

$\dot{q}_{chem}$

T_f

T_{crit}

T_{oxid}

T_{amb}

$\dot{q}$
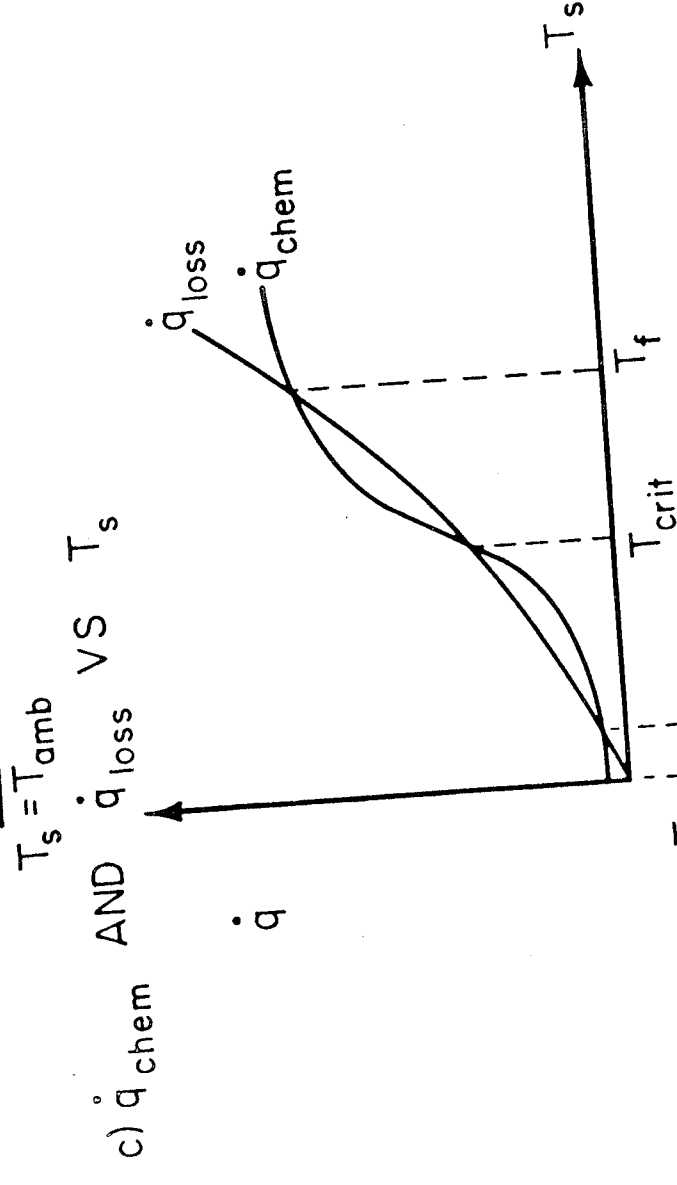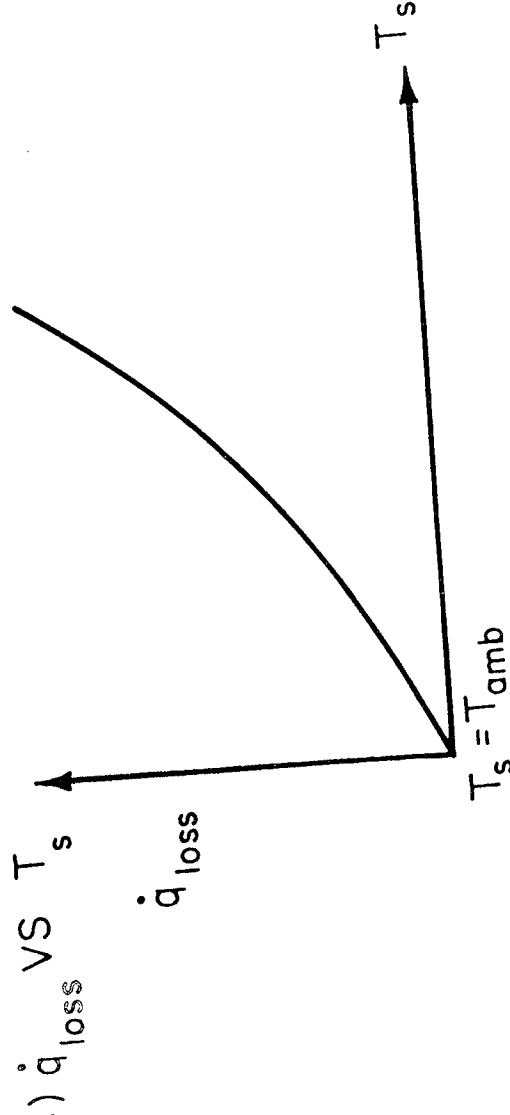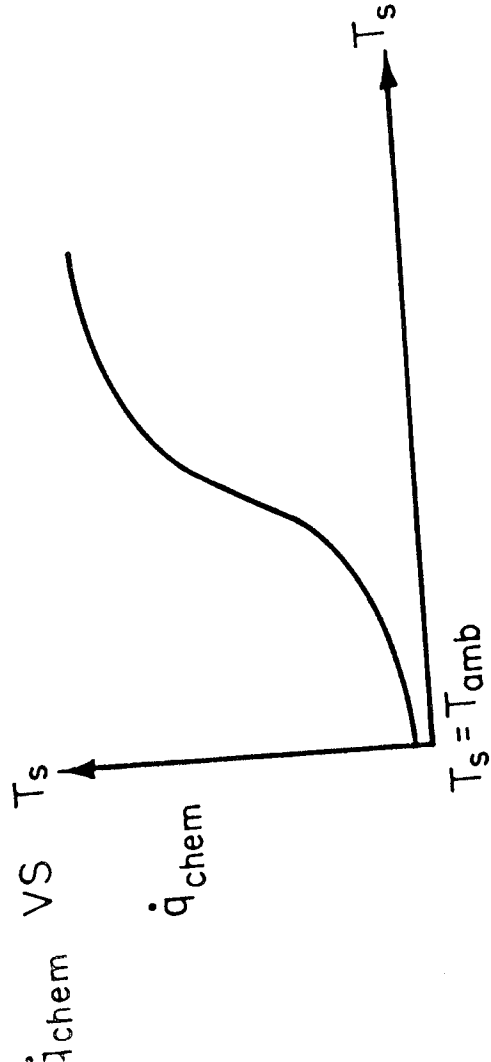
HETEROGENEOUS IGNITION:
RATE OF CHEMICAL ENERGY RELEASE AND RATE
OF HEAT LOSS VS SURFACE TEMPERATURE

$\partial T / \partial r$ = temperature gradient evaluated at the surface of the particle ($r = r_o$) either into the fuel ($r = r_{o-}$) or into the oxidizer ($r = r_{o+}$), $^{\circ}K/cm$;

ϵ = total surface emissivity, dimensionless;

σ = Stephen-Boltzmann constant, $cal/cm^2 \cdot sec \cdot (^{\circ}K)^4$;

T_r = effective radiating temperature of the environment, $^{\circ}K$.

The general form of the $\dot{q}_{loss}$ vs T_s curve as obtained from the addition of these three heat loss terms is depicted in Fig. 2b. Notice that at the origin, where T_s is equal to the ambient gas temperature T_{amb}, $\dot{q}_{loss}$ is equal to zero. In order that this be true, it is necessary that the overall temperature (both internal and surface) of the sample be equal to T_{amb} before heating begins. If T_{amb} is taken to be room temperature ($298^{\circ}K$), then this becomes a perfectly reasonable approximation of an actual physical heating process. In other words, for convenience, the heating of the sample is considered to take place in a room temperature environment in which the original temperature of the sample is also $298^{\circ}K$. Thus if $T_s = T_{amb} = 298^{\circ}K$, then $\dot{q}_{loss}$ is equal to zero since only then is $\dot{q}_{cond,f}$ equal to zero.

Other values of T_{amb} can also be considered, but it is felt that this example is the easiest to visualize; indeed the curves can quite simply be extended to other values of T_{amb}, as will be made clearer in a discussion of Fig. 3 at the end of this section.

If the most general case is considered, the $\dot{q}_{chem}$ and $\dot{q}_{loss}$ curves may be combined in the fashion depicted in Fig. 2c in which three points of intersection defining equilibrium conditions at the sample surface are obtained. The end points of intersection at the low and high temperature regions of Fig. 2c are both <u>stable</u> equilibrium temperatures with respect to small perturbations of the surface temperature T_s since:

$$\left. \left(\frac{\partial \dot{q}_{chem}}{\partial T_s} \right) \right|_{T_s = T_{oxid}} < \left. \left(\frac{\partial \dot{q}_{loss}}{\partial T_s} \right) \right|_{T_s = T_{oxid}} \tag{II-8}$$

and

$$\left(\frac{\partial \dot{q}_{chem}}{\partial T_s}\right)\Bigg|_{T_s = T_f} < \left(\frac{\partial \dot{q}_{loss}}{\partial T_s}\right)\Bigg|_{T_s = T_f} \qquad \text{(II-9)}$$

Physically this means that at temperatures somewhat greater than T_{oxid} or T_f, $\dot{q}_{loss}$ is greater than $\dot{q}_{chem}$ and thus T_s tends to decrease; at temperatures somewhat less than T_{oxid} or T_f, $\dot{q}_{loss}$ is less than $\dot{q}_{chem}$ and T_s tends to increase. Therefore T_{oxid} and T_f are stable temperatures to which the system tends to converge.

The high temperature intersection T_f physically represents the flame temperature and is then the steady-state self-sustained combustion mode of the system. As mentioned previously, for metals, the flame temperature is limited by enthalpy considerations to the boiling point of the metal oxide.

The low temperature intersection T_{oxid} is referred to as the oxidation temperature. It physically represents the ordinary slow, kinetically controlled, surface oxidation reaction common at this low temperature. However, as can be seen by the fact that the $\dot{q}_{chem}$ and $\dot{q}_{loss}$ curves are nearly tangent at T_{oxid}, the true oxidation process realistically occurs over a short temperature range (12).

The center point of intersection, denoted by T_{crit}, is called the critical temperature and is an unstable equilibrium surface temperature since:

$$\left(\frac{\partial \dot{q}_{chem}}{\partial T_s}\right)\Bigg|_{T_s = T_{crit}} > \left(\frac{\partial \dot{q}_{loss}}{\partial T_s}\right)\Bigg|_{T_s = T_{crit}} \qquad \text{(II-10)}$$

Thus surface temperatures less than T_{crit} tend to decrease to T_{oxid} since here $\dot{q}_{loss}$ is greater than $\dot{q}_{chem}$ and surface temperatures greater than T_{crit} tend to increase to T_f since here $\dot{q}_{loss}$ is less than $\dot{q}_{chem}$. It is the latter of the above situations that is so important in this development, i.e., once the critical temperature is reached, the system tends to higher temperatures. Because this phenomenon is so vital to a com-

plete understanding of the ignition problem, the critical temperature T_{crit} is defined as follows: T_{crit} is the lowest initial surface temperature from which the surface may self-heat to reach the steady-state combustion configuration.

The critical temperature is commonly called the spontaneous ignition temperature in the literature. It is here labeled the critical temperature in order to avoid confusion with the experimental ignition temperature shortly to be discussed. The existence of this critical temperature is the basic cause of the metal dust explosions that on occasion occur in various industrial plants.

It is now important to define an ignition temperature T_{ign} which can be easily related to the experimental ignition temperature. For most systems, the experimental ignition temperature is usually taken to be that temperature at which the flame appears. When the flame appears, whether it be vapor-phase or surface combustion, there occurs simultaneously the most rapid rate of change with time of both light intensity and sample temperature.[3] Since temperature runaway is the most obvious phenomenon of the ignition process and since it is the easiest to measure, especially for metals which burn of the surface, it is convenient to define a theoretical ignition temperature in terms of this particular property of the ignition process.

Now, since the aforementioned control colume is assumed to be at a uniform temperature T_s, the time rate of change of the surface temperature can be expressed as a linear function of the quantity $(\dot{q}_{chem} - \dot{q}_{loss})$ as follows:

$$\rho \, \delta \, C_p \, \frac{\partial T_s}{\partial t} = \dot{q}_{chem} - \dot{q}_{loss} \qquad \text{(II-11)}$$

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[3] In the course of many experiments with various metals, the maximum change of light intensity and temperature appear to always coincide.

where

ρ = density of the fuel, g/cm^3;

δ = thickness of the control volume ($\delta \neq 0$), cm;

c_p = fuel specific heat, $cal/g \cdot {}^{\circ}K$.

According to Eq. (II-11) then, the ignition temperature can be defined by that point at which the maximum difference between $\dot{q}_{chem}$ and $\dot{q}_{loss}$ exists. Now since the ignition temperature must be above the critical temperature, and below the flame temperature, then the ignition temperature T_{ign} can be represented graphically as in Fig. 3.[4]

Mathematically, the ignition temperature is defined by looking for the maximum value of $(\dot{q}_{chem}-\dot{q}_{loss})$ above T_{crit} but below T_f. Therefore:

$$\frac{\partial}{\partial T_s}\left(\dot{q}_{chem} - \dot{q}_{loss}\right)\Big|_{T_s=T_{ign}} = 0 \qquad \text{(II-12)}$$

where

$$T_{crit} \leq T_{ign} \leq T_f \qquad \text{(II-13)}$$

Thus the full definition of the experimental ignition temperature becomes the following:

$$\left\{ \begin{array}{l} \left(\dfrac{\partial \dot{q}_{chem}}{\partial T_s}\right)\Big|_{T_s=T_{ign}} = \left(\dfrac{\partial \dot{q}_{loss}}{\partial T_s}\right)\Big|_{T_s=T_{ign}} \\ T_{crit} \leq T_{ign} \leq T_f \end{array} \right\} \qquad \text{(II-14)}$$

The above then points out the theoretical difference between T_{crit} and T_{ign} as interpreted on a $\dot{q}$ vs T_s diagram. At T_{crit}, the magnitudes of $\dot{q}_{chem}$ and $\dot{q}_{loss}$ are equal; at T_{ign}, the slopes of the $\dot{q}_{chem}$ and $\dot{q}_{loss}$ curves are equal. Physically, this distinction that has been introduced between the ignition temperature and the critical or spontaneous ignition temperature is a very important one, since it allows for the distinct

[4]In this graph, the internal coordinate system is identical to Fig. 2c.

possibility of the existence of an ignition delay time. This possibly long self-heating time is what must be prevented when metal particles are used to increase the performance of rocket combustion chambers, for example. Thus, in these applications, the ignition temperature, not the critical temperature, is of prime importance in dealing with ignition inefficiencies.

As intimated above, the ignition delay time in metal ignition may be of the order of minutes rather than a few seconds or milliseconds as in a homogeneous gaseous ignition process. This large difference in ignition delay time between heterogeneous and homogeneous systems is essentially due to the need for oxidizer diffusion to, and adsorption on, the fuel surface in the case of a heterogeneous chemical reaction. If the rate of chemical heat input, $\dot{q}_{chem}$, for a heterogeneous system is represented in Arrhenius form, as for a homogeneous system, then the computed values of $\dot{q}_{chem}$ will indicate the influence upon heterogeneous reaction of the physical processes of diffusion and adsorption. The much lower value of $\dot{q}_{chem}$ for a heterogeneous system, as compared to that in a homogeneous system, accounts for the large ignition delay time for such reactions, since $\partial T / \partial t$ is a linear function of $(\dot{q}_{chem} - \dot{q}_{loss})$ for homogeneous as well as heterogeneous systems.

Now, for both homogeneous and heterogeneous systems in the kinetic range, $\dot{q}_{chem}$ and thus the ignition delay time is a strong function of the kinetic frequency or pre-exponential factor, if the appropriate reaction rate is expressed in Arrhenius form (19). On the basis of collision theory, it has

been found that in general the more complicated the chemical reaction process, the smaller in magnitude is the kinetic frequency factor and thus the slower is the reaction rate (20). For homogeneous bimolecular reactions, the frequency factor is on the order of 10^{10} to 10^{14} cm^3/mole-sec and for unimolecular reactions, around 10^{13} to 10^{17} sec^{-1} (19,20). For heterogeneous reactions, the pre-exponential factor has a value for metal systems of 10^{-3} to 10^{-8} gm^2/cm^4-sec for protective oxide systems and 10^{-1} to 10^{-6} gm/cm^2-sec for non-protective oxide systems (21,22). Thus for a complicated heterogeneous metal reaction, $\dot{q}_{chem}$ is much smaller in magnitude; in addition, there is a further reduction of $\dot{q}_{chem}$ and thus a longer ignition delay time for a heterogeneous reaction due to the onset of the diffusional control of the reaction rate at higher surface temperatures.

Fig. 3 displays all of the above defined surface temperatures on a diagram covering the entire temperature range starting at $0^{\circ}K$. The internal coordinate system has its origin at $\dot{q}=0, T_s=T_{amb}$ and is the coordinate system used in Fig. 2. However, the extension to $0^{\circ}K$ is made here in order to discuss some of the properties of the heterogeneous ignition system in more detail.

At $0^{\circ}K$, $\dot{q}_{chem}$ goes to zero; this is appropriate since at lower temperatures the molar reaction rate $\dot{m}$ which is a factor in determining $\dot{q}_{chem}$, is in the kinetic regime and as T_s goes to zero, indeed the exponential term in Eq. (II-4) approaches zero thereby forcing $\dot{m}$ and thus $\dot{q}_{chem}$ to also approach zero. As discussed previously $\dot{q}_{loss}$ approaches zero as T_s approaches T_{amb} if the temperature of the sample before heating (at $t=0^-$) is also T_{amb}. The ambient temperature is usually taken to be $298^{\circ}K$ since the process is much easier to visualize at room temperature. However, any other value of T_{amb} may be used, but the initial temperature of the sample must also be raised to T_{amb} in order that $\dot{q}_{loss}$ be equal to zero at T_{amb}. This may seem very artificial, but again, it is done in this manner
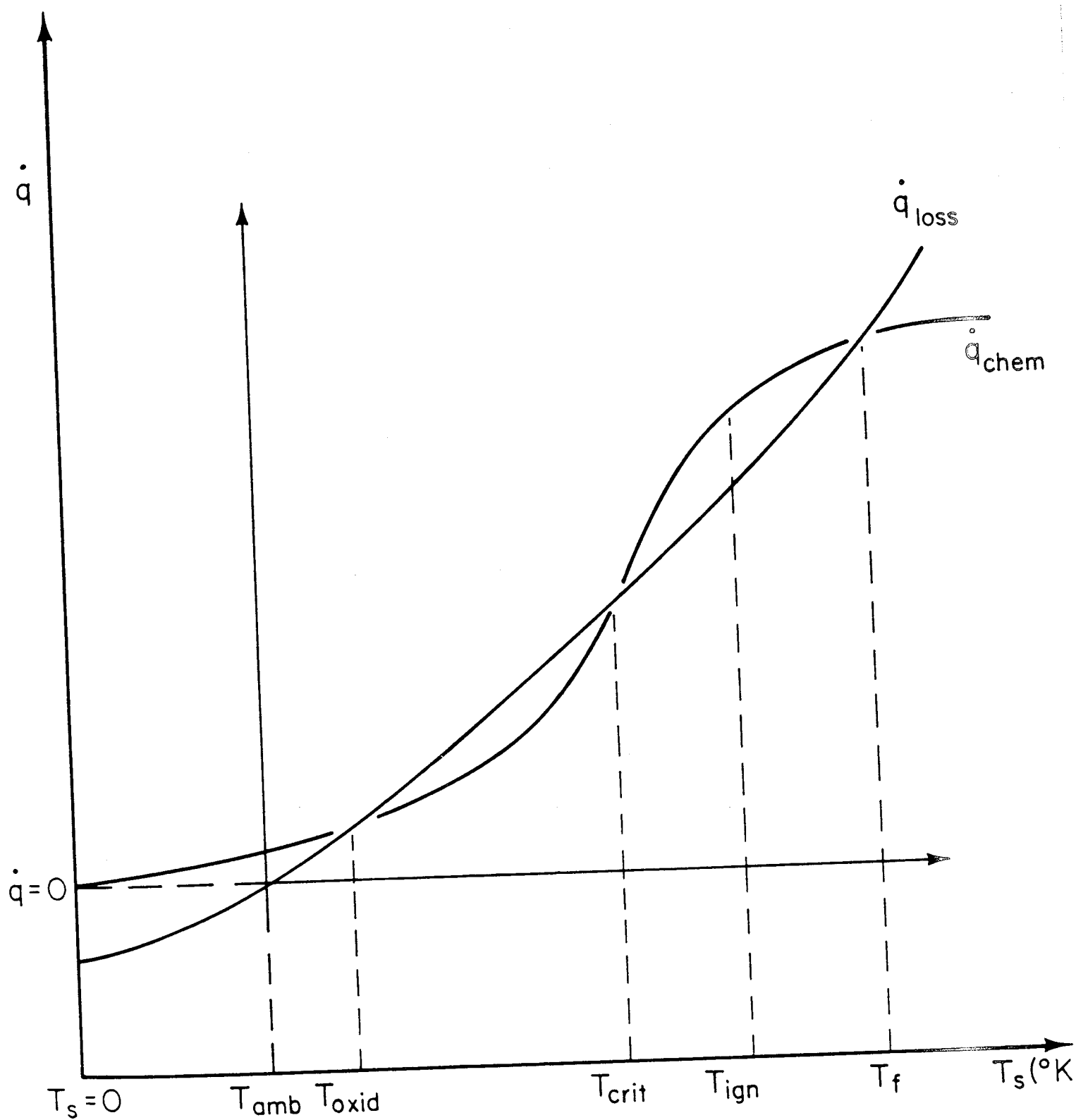
HETEROGENEOUS IGNITION :
COMPLETE VARIATION WITH TEMPERATURE

FIGURE 3

simply for the sake of clarity in the development of the model.

More importantly however, the ambient temperature is taken to be $298^{\circ}K$ because this will give the most general results in terms of the three points of intersection shown in Fig. 2c. In other words, by varying T_{amb} for a fixed value of T_s, $\dot{q}_{chem}$ stays essentially constant while $\dot{q}_{loss}$ varies a great deal and thus it is possible that only one point of intersection, either at the low temperature or high temperature end of the scale, will appear. In this case, the sample will either never ignite or always ignite. This situation is not of general interest here and thus T_{amb} is taken to be near room temperature. However, even in this case, if the initial temperature of the sample is kept at the appropriate T_{amb} for the system, then $\dot{q}_{loss}$ is equal to zero at that particular $T_s = T_{amb}$.

In the unsteady problem, $\dot{q}_{loss}$ need not always be equal to zero at $T_s = T_{amb}$. At any constant value of T_s, once the heating process has begun, $\dot{q}_{loss}$ decreases equally over the entire temperature range, due to the conduction losses to the interior of the metal sample (12). In fact, $\dot{q}_{loss}$ takes on negative values at $T_s = T_{amb}$ since now the internal energy of the sample tends to heat the surface because the interior temperature is greater than the surface temperature, and therefore $\dot{q}_{loss}$ actually becomes a heat source. Now, a diagram similar to Fig. 3 can be graphed for any time t* in the heating process. But for any time greater than t=0, $\dot{q}_{loss}$ will not be equal to zero at $T_s = T_{amb}$ since the entire sample has now gained energy from the heating process at a higher surface temperature.

This last paragraph deserves a little more clarification since it implies other details of the model as interpreted here that are not so obvious. Recall that Fig. 3 represents a strictly time-independent system and therefore one must use extreme caution in analyzing for example the variation of

surface temperature with time in an actual physical heating process. This graph then strictly represents the instantaneous attainment of a surface temperature T_s artificially put on the surface of a fuel sample of original overall temperature T_{amb} in a gaseous atmosphere of temperature T_{amb}. This is somewhat analogous to the dumping of a sample in a heat bath in which the sample surface instantaneously attains the bath temperature, except that here there is another variable in that the atmosphere has an independent temperature T_{amb} equal to the overall temperature of the sample at time $t=0^-$.

Now, imagine the sample in equilibrium with the oxidizing atmosphere at T_{amb}. Instantaneously a higher temperature T_s is made to appear on the fuel surface; it remains there until at a later time when instantaneously the original ambient temperature T_{amb} is put on the surface. At this juncture, $\dot{q}_{loss}$ cannot be equal to zero at $T_s=T_{amb}$ since the interior of the sample is not at temperature T_{amb}, but at a higher temperature, which tends to heat the surface thus making $\dot{q}_{loss}$ a negative quantity since indeed this process represents a heat gain. Therefore, all the diagrams in this report represent steady-state situations at time $t=0^+$ when $\dot{q}_{loss}$ is equal to zero at $T_s=T_{amb}$.

Not only is this done for better visualization of the actual theoretical ignition process, but also for a much more practical reason. The essential use for these diagrams is to be able to predict if a fuel sample will or will not ignite. If it does not ignite, it must stabalize at T_{oxid}; if it does ignite, it must reach T_f. Although the actual values of T_{oxid} and T_f will vary with time somewhat (12), whatever values they represent will eventually be reached in the final steady-state configuration of the fuel sample. In application, the main query is to whether or not the sample will ignite with a given set of initial conditions on the problem. Therefore the determination of whether or not ignition will take place must be

answered practically at time $t=0^+$, which is really the main reason for graphing these curves at this particular value of time.

Looking again at the $\dot{q}_{loss}$ curve in Fig. 3, it can be seen that at $T_s < T_{amb}$, $\dot{q}_{loss}$ becomes an actual heat gain even at time $t=0^+$. This is again true because at $T_s < T_{amb}$, the interior temperature of the sample is greater than the surface temperature.

Also, because $\dot{q}_{loss}$ is equal to zero at T_{amb}, then for this case in which there is no solid phase product deposited on the sample surface, the stable low-temperature oxidation temperature T_{oxid} is somewhat higher than T_{amb}. Although this may seem peculiar in light of practical experiences with metals, there is a fairly simple explanation that will be discussed in detail in the following section.

2. Heterogeneous Ignition with Solid-Phase Reaction Products

All of the preceeding has been for the case where the products of combustion appear in the gas phase. For metals, the greatest difficulty comes about through the fact that a solid state metal oxide coating appears on the surface of the sample. This represents one more level of difficulty in the treatment of the heterogeneous ignition problem.

Again a spherical fuel sample in a static oxidizing atmosphere is considered. The control volume includes those products formed on the reaction surface. In addition, the product temperature is uniform and equal to the surface temperature so that the solid-phase products do not contribute to the heat transfer characteristics of the configuration. Indeed, all the assumptions of the previous section are maintained such that the equations and concepts developed there remain valid for the case of solid-phase product formation.

It has been well-established in isothermal oxidation experiments that, in general, at low temperatures, the presence of the metal oxide film leads to the so-called protective oxidation rate laws while at higher temperatures, the product

film offers no protection to further oxidation and the linear rate law is observed (21,23,24).[5] These rate laws in general are of the form:

$$dx/dt = k_n / x^{n-1} \qquad \text{(II-15)}$$

where

    x = mass of oxygen consumed per unit surface area at time t, gm/cm^2;

    k_n = rate constant, $(gm/cm^2)^n/sec$;

    n = oxidation law index, dimensionless.

The variable x may alternatively represent the mass of metal transformed to the oxide or the thickness of the oxide layer in the case of a uniform, plane parallel oxide film. However, the amount of oxygen consumed in the oxidation process per unit surface area is most widely applicable to metals of interest and most measurements of the rate constant have been made in this form (21,22).

Integration of equation (II-15) with n=2 or n=3 gives respectively the parabolic or cubic protective rate law:

$$x^2 = 2k_2t + C_2 \quad ; \qquad \text{(II-16)}$$

$$x^3 = 3k_3t + C_3 . \qquad \text{(II-17)}$$

The logarithmic law is another common example of a protective rate law:

$$x = k \ln t + C \qquad \text{(II-18)}$$

Integration of equation (II-15) with n=1 gives the linear rate law:

$$x = k_1 t + C_1 \qquad \text{(II-19)}$$

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[5] See these same references for a discussion of the microscopic mechanisms behind these laws.

In contrast to the protective rate laws (parabolic, cubic, logarithmic), for which the rate of reaction dx/dt decreases with time, the rate of reaction for linear oxidation is independent of time and is thus independent of the amount of gas or metal previously consumed in the reaction. In other words, here the rate of reaction is independent of the amount or thickness of the oxide film on the sample. One explanation of this phenomenon that is most usually experimentally observed (21,23) is that the oxide film has either become porous or has cracked so that the metal surface is not protected from the oxidizing atmosphere.

In most circumstances the parabolic protective oxidation rate law appears at average temperatures; as the temperature increases, the non-protective linear rate law usually appears before ignition occurs. Thus at lower temperatures, the heterogeneous reaction rate is inhibited by this product film, while at higher temperatures, the reaction rate is essentially independent of the product film. Now the temperature at which this changeover occurs is called the transition temperature, T_{trans}. It is the lowest temperature above which the metal-oxidizer system is controlled by a linear oxidation rate law that persists until metal ignition occurs.

Now, since below this transition temperature the metal is protected, the transition temperature must be less than or equal to the ignition temperature. In fact the transition temperature is the lowest possible ignition temperature for any metal-oxidizer system. This fact will become clearer in the next section.

Mellor (12) attributed the appearance of the transition temperature to a phase change or other changes leading to stress or thermal cracking of the oxide film or perhaps melting of the oxide as in the case of aluminum. Now the linear rate law may not only be due to the non-protectiveness of the oxide layer as intimated by the above mechanisms, but may also arise from other physical mechanisms such as a non-porous barrier layer

between the metal substrate and a porous outer oxide layer (12,23). Therefore, the transition temperature only defines the appearance of a <u>nonprotective</u> linear rate law which persists at all higher temperatures between T_{trans} and T_{ign}.

In view of the significance of the transition temperature in defining the effect of the solid oxide layer in metals, this problem may be graphically analyzed via an uncomplicated extension of the simpler problem of heterogeneous ignition with gas-phase reaction products as displayed in Fig. 2c. At lower temperatures the molar reaction rate $\dot{m}$ will be reduced due to the presence of the protective product film. Since $\dot{m}$ here is in the kinetic regime, $\dot{q}_{chem}$ will decrease following Eqs. (II-1) and (II-4) due to a decrease in the pre-exponential factor and an increase in the activation energy. At temperatures above T_{trans}, $\dot{q}_{chem}$ is assumed to approach the value for a clean surface although this is not strictly true in the real case since some oxide always adheres to the exterior of the metal. The $\dot{q}_{loss}$ curve remains the same since the solid oxide coating has been included in the control volume.

Consider now the region near the critical temperature which represents the area of changeover from high temperature oxidation to ignition and subsequent steady-state combustion. Fig. 4a depicts this region for the case of <u>no</u> solid-phase product formation. Figs. 4b and 4c depict the case of solid-phase product formation for the two possible subcases: $T_{trans} < T_{crit_0}$; $T_{trans} > T_{crit_0}$ where T_{crit_0} is the original critical temperature for the clean surface.[6] From these graphs, a criterion for metal ignition may be proposed:

$$\text{If } T_{trans} < T_{crit_0}; \text{ then } T_{ign} \geq T_{crit_0} ; \qquad \text{(II-20)}$$

$$\text{If } T_{trans} > T_{crit_0}; \text{ then } T_{ign} \geq T_{trans}. \qquad \text{(II-21)}$$

If $T_{trans} < T_{crit_0}$, then the ignition temperature is called

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[6] The $\dot{q}_{chem}$ curve for the clean surface is represented in these figures by the dashed line.

a) NO SOLID-PHASE PRODUCT
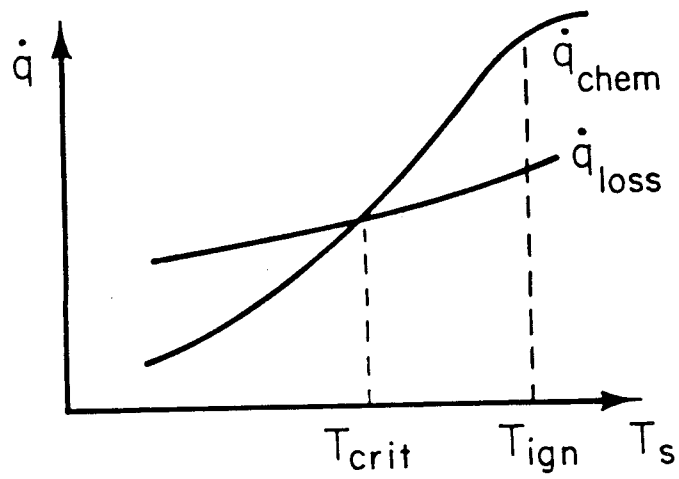
b) $T_{trans} < T_{crit_o}$
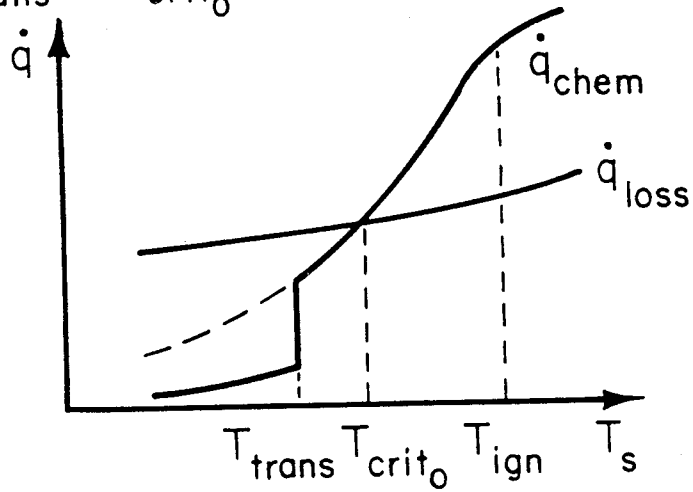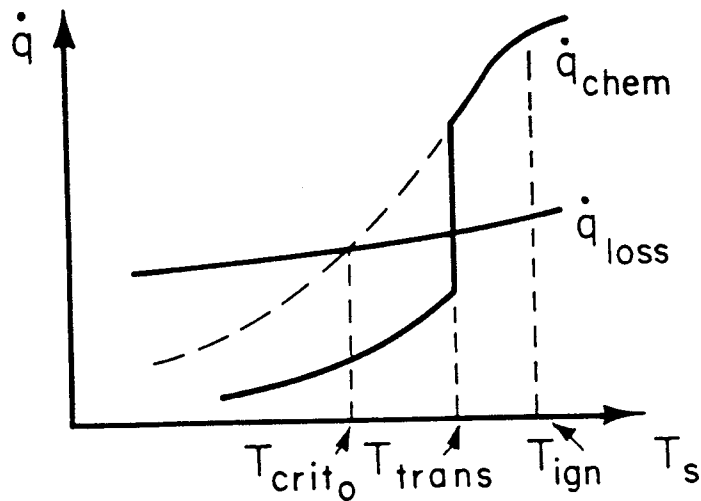
c) $T_{trans} > T_{crit_o}$

THE IGNITION CRITERION

FIGURE 4

critical temperature controlled, whereas if $T_{trans} > T_{crit_o}$, the ignition temperature is called transition temperature controlled. Most metals are critical temperature controlled, while a few metals such as aluminum and beryllium are thought to be transition temperature controlled.

It is important to note here that a transition temperature controlled metal sample of reasonable size cannot in general self-heat to ignition. This statement is supported by the fact that an impervious oxide layer covering the bare metal should protect the surface from producing a large neat of reaction until $T_s \geq T_{trans}$. Thus, the sample would be expected to stabilize at T_{oxid} for all original $T_s \leq T_{trans}$. In order that this occur, it is necessary that the actual critical temperature, as determined by the protective surface (the solid rather than the dashed curve in Fig. 4c) be greater than T_{crit_o}, but not less than T_{trans}, so that self-heating may not occur below T_{trans}. In other words, $\dot{q}_{loss}$ must be greater than $\dot{q}_{chem}$ for all $T_s \leq T_{trans}$ and necessarily $T_{trans} = T_{crit}$ for the oxide-protected surface of the bulk metal as depicted in Fig. 4c.

Mellor (12), in his original model, did not have the $\dot{q}_{chem}$ and $\dot{q}_{loss}$ curves arranged as in Fig. 4c, but instead had $\dot{q}_{chem}$ greater than $\dot{q}_{loss}$ for some higher surface temperatures less than T_{trans} and thus had T_{crit} less than T_{trans} making it possible for a transition temperature controlled metal to self-heat to ignition. Although this may be true for metal particles where $\dot{q}_{loss}$ becomes extremely small[7], it is in general not true as stated previously for reasonably sized samples. This overall behavior corresponds for example to the physical situation of the known transition temperature controlled metal, aluminum, which is very well protected at temperatures below T_{trans} by the metal oxide, and is not known to ignite via self-heating from a lower temperature except perhaps for particle-sized samples as indicated above (13, 25, 26).

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[7]See section 3 of this chapter for a more detailed discussion of this point.

In order to summarize the effects of T_{trans} on all previously defined temperatures of interest, it is necessary to study in detail Fig. 5. Fig. 5 is an extension of Fig. 3 to the case of a heterogeneous reaction with a solid-phase oxide product. The typical decrease in $\dot{q}_{chem}$ below T_{trans} for both a critical and a transition temperature controlled metal is shown here but with emphasis on the critical temperature controlled subcase (the T_{trans} controlled subcase is represented by the dashed $\dot{q}_{chem}$ curve). For this subcase, there is theoretically no change in T_{crit}, as well as no change in T_{ign} and T_f, from the case of a heterogeneous reaction with gas-phase reaction products.

For both subcases, the protective quality of the low temperature oxide film results in a significant lowering of the oxidiation temperature from T_{oxid_O} to T_{oxid}. The original value of the oxidation temperature T_{oxid_O} is, as mentioned in the previous section, somewhat higher than the ambient temperature, T_{amb}. However, due to the protective qualities of the oxide layer, the new value of the oxidiation temperature T_{oxid}, is postulated to be very near T_{amb}, as would physically be expected for most metals. For example, calcium is known to get fairly warm if exposed to a room temperature environment, and would be expected to stabilize to some temperature higher than T_{amb} if the oxide coating were continually removed during the oxidation reaction. However, it is also a matter of experience that calcium quickly develops a protective oxide coating and that after some time, the temperature stabilizes close to T_{amb}. Also, since some metal oxides, such as Al_2O_3, are more protective than others, then metals like aluminum stabilize extremely close to room temperature and thus do have $T_{oxid} \approx T_{amb}$ as shown in Fig. 5.

In summary then, a transition temperature has been defined which separates regions of time-dependent and time-independent reaction rates for heterogeneous metal-oxidizer
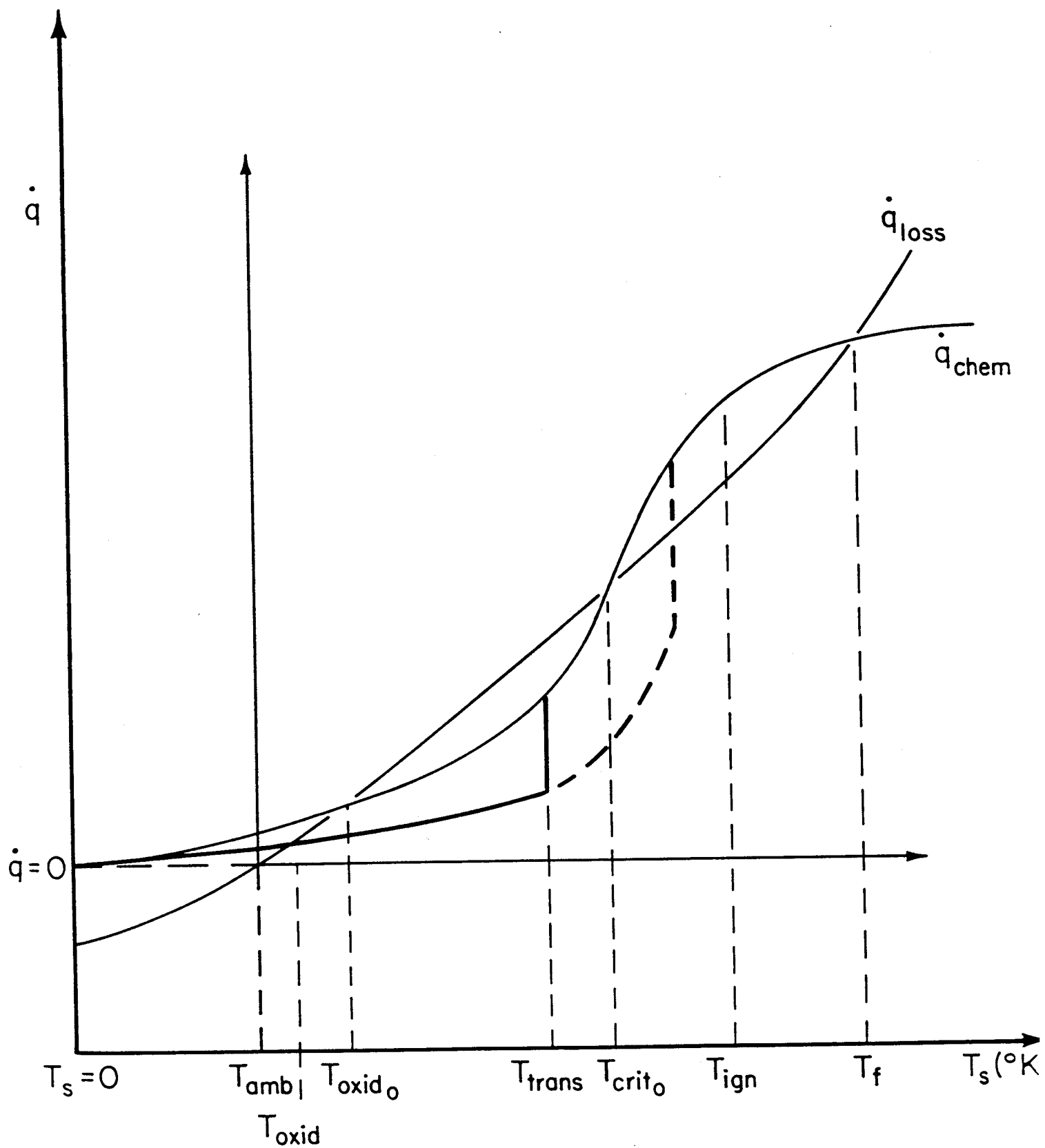
THE LOW TEMPERATURE EFFECTS OF
THE TRANSITION TEMPERATURE

FIGURE 5

systems. Ignition is postulated to occur only after this temperature is exceeded and furthermore, the ignition process occurs exactly as in other heterogeneous systems.

3. Application of the Steady-State Model to Metal Pyrophoricity

One of the more interesting properties of metals is the ability of a well-dispersed group of small metal particles to spontaneously ignite when exposed to an oxidizer at room temperature. Although this is a difficult problem to analyze because of the cooperative effort between the particles to minimize the rate of heat loss, it is still possible to study instead the effect of metal sample size on the ignition temperature of a single particle. Such studies have indeed been made on this pyrophoric behavior of metal particles, and it has been concluded that a decrease in sample size generally results in a decrease in ignition temperature. It is of interest here to attempt to explain this phenomenon in terms of the present model of metal ignition. First, however, an overall discussion of this problem seems appropriate.

In order for a metal particle to be able to first, self-heat, and second, self-heat to a fairly low ignition temperature, it is necessary that the total heat release increase with respect to the total heat loss as metal particle size is reduced. Now, as particle size decreases, sample surface area increases with respect to sample volume; that is, the ratio of surface area to volume of the sample (S/V, a suitable size index) increases. This increase in S/V is indicative of a relative increase in the total chemical heat release with respect to the total heat capacity of the fuel particle. Therefore, pyrophoric action can be attributed to an increase in the amount of free surface of the metal, since this is responsible for the inability of the metal particle to dissipate its heat of oxidation rapidly enough, because

with more surface area and less volume, more heat is liberated that cannot be dissipated by the metal particle itself.

Of course, the heat of oxidiation of the metal will be greatly reduced by a protective oxide coating and thus, a metal with a low transition temperature which in all probability it is then a critical temperature controlled metal will tend to be more pyrophoric. Of these critical temperature controlled metals, those which have the highest heat of

TABLE 1
HEATS OF FORMATION OF PREDOMINATING METAL OXIDES[*]

Oxide	$-\Delta H_f^{298}$	Oxide	$-\Delta H_f^{298}$
Ta_2O_5	488.80	SnO_2	142.01
Al_2O_3	400.40	SrO	141.10
V_2O_5	381.96	WO_2	140.94
B_2O_3	303.64	Bi_2O_3	139.00
ThO_2	293.20	BaO	133.50
Cr_2O_3	272.65	ZnO	83.25
HfO_2	266.05	FeO	63.50
ZrO_2	261.50	CdO	62.20
UO_2	259.20	NiO	57.30
TiO_2	225.50	CoO	57.10
SiO_2	217.50	PbO	50.39
MoO_3	182.65	Cu_2O	41.80
MgO	143.70	Ag_2O	7.20
BeO	143.10	Au_2O_3	0.80

*Data in kcal/gmole taken from Refs. (17,21,28)

Eqs. II-1, II-2, II-4), then as S/V increases, the critical temperature will decrease, thus theoretically making it possible for a metal sample to self-heat to ignition from a lower value of the initial surface temperature.

Recall that it has been previously postulated that a metal has its ignition temperature controlled by either its critical or transition temperature depending on whether T_{crit} is greater than or less than T_{trans}. Since the transition temperature is here assumed to be independent of sample size, a transition temperature controlled metal is postulated to have its ignition temperature independent of sample size even though its critical temperature is not, while a critical temperature controlled metal has both its critical and ignition temperatures decrease with a decrease in metal sample size.[9] In short then, metals whose ignition is controlled by T_{crit} will experience a size effect while metals whose ignition is controlled by T_{trans} will experience no size effect.

It is interesting to note that as sample size is reduced, and thus $\dot{q}_{loss}$ is decreased, the metal-oxidizer system will shift from a critical temperature controlled system (Fig. 4b) to the appropriate transition temperature controlled system (Fig. 4c). As the particle size is further decreases, it is possible as mentioned in the previous section to have $\dot{q}_{loss}$ become so small that T_{crit} becomes less than T_{trans} and therefore the sample may self-heat from temperatures below T_{trans} to eventual ignition. Indeed, it might perhaps be possible that such a process occur for a transition temperature controlled metal of bulk size, but here the sudden increase in $\dot{q}_{chem}$ at T_{trans} is usually much larger and the ignition temperature is thus maintained at its bulk value.

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[9] See Mellor (12) for a mathematically orientated argument that outlines the influence of T_{crit} and T_{trans} on the ignition temperature.

When the size of a metal particle has decreased to the point where the system, which was critical temperature controlled in the bulk regime, is now transition temperature controlled, any further decrease in sample size will have little effect on the ignition temperature, as in any transition temperature controlled situation. In other words, as the particle size decreases, the critical temperature will continue to decrease; however, the ignition temperature will never become less than the appropriate transition temperature for that system.

Turning for a moment to the bulk regime, it is postulated that once the sample reaches a certain bulk size, in reference to the surface, the sample volume is infinite. Thus, the $\dot{q}_{loss}$ curve will tend to stabilize and consequently the critical and ignition temperatures will tend to remain relatively constant with further increases in size.

In summary then, for metals whose bulk ignition is controlled by the critical temperature, the ignition temperature will decrease with decreasing sample size due to a decrease in the critical temperature. For large samples, the ignition temperature is equal to the bulk ignition temperature; in this regime, the critical and ignition temperatures are relatively independent of size. For intermediate-sized samples, the critical and ignition temperatures will decrease with decreasing sample size until the latter nears the transition temperature. Upon further reduction in sample size, the critical temperature continues to decrease, but the ignition temperature remains relatively constant and approaches the transition temperature. This then is the problem of pyrophoricity, where a small particle may self-heat to the transition temperature and thus ignition, but where a larger sample is not allowed to undergo this physical

process.

One of the more notable achievements of this theory is the prediction of the size effect as demonstrated by Mellor with the aid of an induction furnace facility and two critical temperature controlled metals, magnesium and calcium (12). The induction furnace, which will be described in detail in Chapt. III, accentuates the size effect since it heats on the surface of the sample as is done in the model, and thus makes the conduction losses into the sample very important. In other experimental environments where the metal sample is heated uniformly, it is expected that the size effect will be diminished if the source of the size effect has been correctly assumed to be the conduction heat loss into the metal.

Figs. 6 and 7 demonstrate clearly the size effect in various oxidizing atmospheres at 300 torr for the two metals, magnesium and calcium. Unfortunately, it was not possible in both cases to obtain metal samples with a larger S/V ratio because of the difficulties with industrial production of thin sheets of such metals(12). However, the general trend can be seen on these graphs and furthermore, it appears that the ignition temperature may indeed be minimized by the appropriate transition temperature for the metal under consideration.

4. The Need for Further Experimental Work

Although Mellor contributed a theory applicable to most metals, his experimental work, although fairly extensive, only dealt with the two aforementioned metals, magnesium and calcium. In spite of working with only these two critical temperature controlled metals, Mellor made several final experimental conclusions, based on a long series of experiments to find both the ignition and critical temperatures of these metals, and the influence of various parameters on these particular temperatures(12): (1)The ignition temperature is greater than the critical temperature. (2)The minimum possible ignition temperature is the transition temperature. (3)The size effect is lessened in resistance type furnaces

FIGURE 6
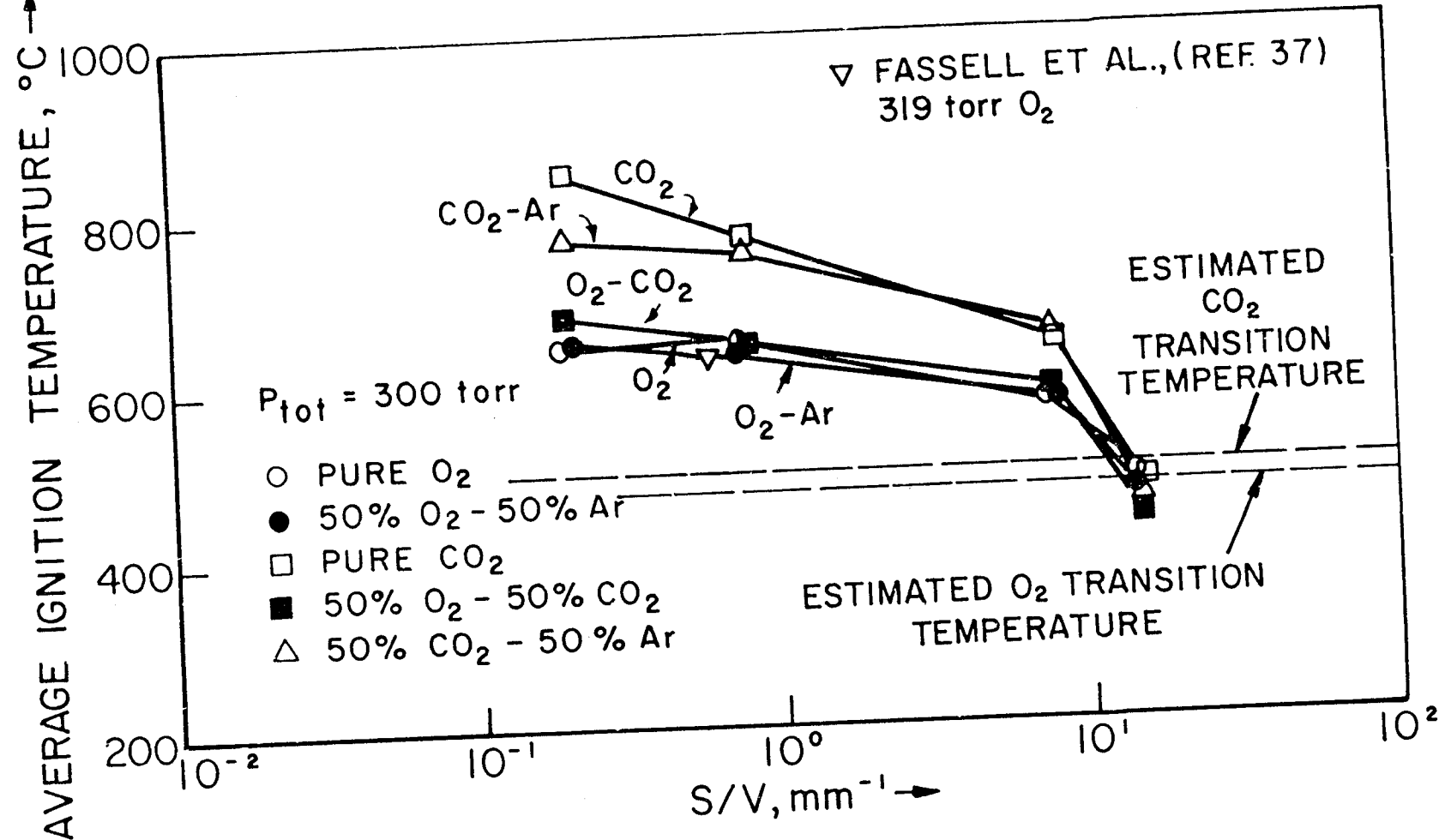
MAGNESIUM AVERAGE IGNITION TEMPERATURE IN VARIOUS OXIDIZING GASES VS SURFACE TO VOLUME RATIO (TOTAL PRESSURE = 300 torr)
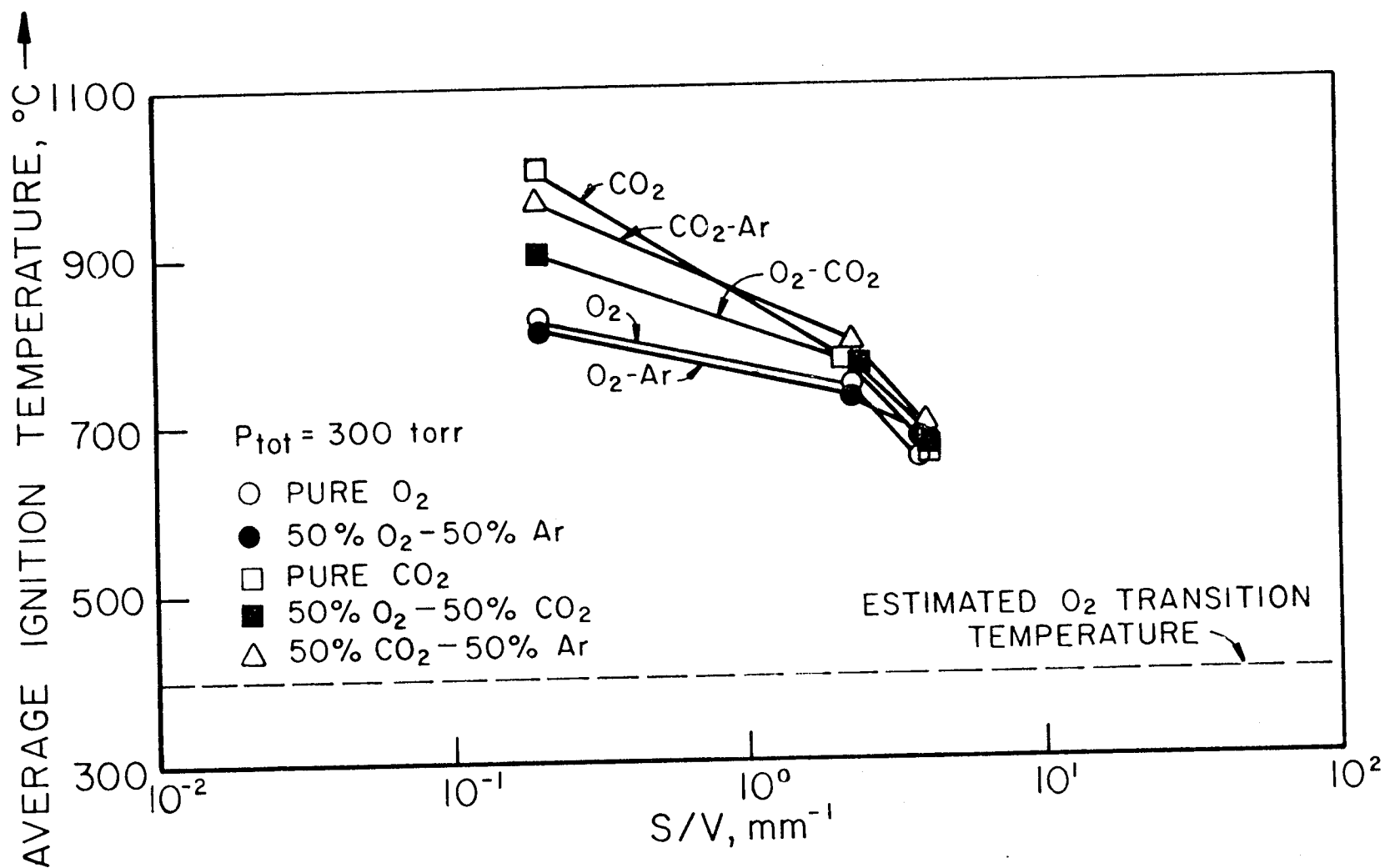
CALCIUM AVERAGE IGNITION TEMPERATURE IN VARIOUS OXIDIZING GASES VS SURFACE TO VOLUME RATIO (TOTAL PRESSURE = 300 torr)

FIGURE 7

due to more uniform heating. (4)The heating rate into the sample especially in oxygen atmospheres, has little effect on the ignition temperature of bulk samples, thus implying that the ignition temperature is fairly independent of oxide thickness. (5)The bulk ignition temperature is not absolute but depends on the experimental environment thus making the transition temperature the only absolute reference temperature.

The first three of these conclusions serve to add credance to the present model while the fourth conclusion eliminates one environmental variable from consideration. The fifth statement is the only one that opposes a postulate of the metal ignition model. In Chapt. IV, the reasons why Mellor made this statement will be discussed and evidence will be shown as to why this statement is now thought to be false.

Because of the limited range of the experimental work done by Mellor and the lack of information concerning the ignition of metals, it was necessary to undertake three principal modes of development immediately available in order that the ignition phenomena may be further understood, both theoretically and experimentally.

First, because Mellor worked only with critical temperature controlled metals, it was deemed necessary to work with a transition temperature controlled metal in order to show that such a metal has its ignition temperature independent of sample size. Since beryllium and aluminum are the only two metals that are positively transition temperature controlled, aluminum was chosen not only because beryllium and its oxides are toxic, but because aluminum is used so much in chemical rocket performance applications that knowledge about this one metal is of prime value for industrial purposes.

Secondly, it was thought necessary to obtain experimental information for a large class of metals in order to provide data for perhaps a better model and to develop several

important concepts needed in both theoretical and experimental ramnifications of the present model. This experimental information includes measurements of bulk critical and ignition temperatures and the comparison of the latter to the results of other investigators to determine if indeed a consistent bulk ignition temperature can be defined. Measurements of the ignition temperature can also be used to determine if indeed the transition temperature is a constant and also the extent of the variation of the ignition temperature with pressure. Also important to the understanding of the ignition phenomena were perhap some visual observations of the ignition process for different metals.

Thirdly, it was thought necessary to use all these data to develop in the future a more sophisticated quantitative model based on chemical criteria which could satisfactorily predict metal ignition temperatures in at least pure oxygen atmospheres. This application of the data is admittedly a very difficult problem and as such, most of the work reported here concentrates on the second mode of development, dealing specifically with the experimental measurement of bulk ignition temperatures of various metals. Chapt. IV will discuss both the direct experimental results and also many of the topics listed in the last paragraph which apply the data to other pertinent problems in the field.

The next chapter is devoted to a description of the experiments performed and the apparatus used in such experiments. Many of the experimental difficulties are discussed, specifically those which led to the decision not to consider the first mode of development, dealing with the measurement of bulk ignition temperatures for the transition temperature controlled metal, aluminum.

CHAPTER III: EXPERIMENTAL DESCRIPTION

In the present chapter two main topics will be discussed: (1) The apparatus and materials used in the experimental investigation; (2) The experimental design used in this investigation. In addition, the first section dealing with the induction furnace facility is extended to consider the problem of perhaps a better experimental design for the equipment, especially the work coils, in order to achieve higher ignition temperatures in the future. Indeed, the inability of the present experimental configuration to reach higher temperatures handicaps its uses somewhat and, as discussed in this chapter, represents the principal reason for not being able to ignite aluminum metal. For this reason, the main investigation undertaken here was designed to simply measure the bulk ignition temperature of several low ignition temperature metals and to apply these data to those problems listed under the second mode of development as discussed in the previous chapter.

1. The Induction Furnace Facility

Bulk ignition temperatures, as measured in this investigation, were obtained by induction heating the various metals that came under consideration in these experiments. Induction heating was chosen over resistance heating primarily because of two important characteristics of this heating method. First, it provides predominantly surface heating thus emphasizing pre-ignition oxidation as would be found for example in a rocket combustion chamber. Secondly, an induction furnace allows the use of a nearly room temperature environment that, along with its characteristic surface heating, duplicates experimentally the theoretical environment necessary in the most general form of the present model.

In addition, this type of heating offers several practical advantages over resistance heating: (1) uniform, rapid heating and cooling due to the fact that only the load within the work coil is heated during an experiment; (2) the attainment of higher temperatures as compared to resistance heating, again, because only the load is heated; (3) no mechanical or electrical contacts with the sample because of the use of an electromagnetic field; (4) excellent temperature control brought about by the fact that compared to resistance furnaces, induction furnaces characteristically have very low thermal lags.

The principal disadvantage of induction heating is the unknown consequences upon the surface reaction rate of the so-called skin effect, that is, the concentration of the heating process on the surface of the sample. Although the exact ramnifications of this surface heating phenomenon upon surface oxidation kinetics and thus ignition is unknown, in most cases such effects are considered to be small in light of the many advantages of induction heating (29). This does not, however, answer the question as to whether or not measured ignition temperatures are credible considering the fact that such an RF skin effect does indeed exist.

However, considering the magnitude of the thermal conductivity of most metals, it is thought that surface heating has neglibible effects on thermocouple measurements in cases where the sample is molten before ignition or in cases where the heating rate is not rapid, since in both of these circumstances, it is expected that the internal sample temperatures will be reasonably uniform. In several experiments, Mellor (12) indeed found that thermocouple readings nearest to the center of the sample lagged during the heating process, but that all thermocouples (within experimental accuracy)

simultaneously indicated ignition at essentially the same temperature. Also, bulk ignition temperatures were found not to change if the heating rate was varied over a reasonable range (10-200 $^\circ$C/min). This result again indicates that temperatures measured in this manner are reasonably close to the actual ignition temperatures for metals which undergo both surface and vapor phase combustion.

Before proceeding to a description of the apparatus used here, it is best to consider the method by which an induction system operates. The main heating element is a copper water-cooled work coil that carried a high frequency current, usually powered by an electronic high-frequency generator. In the system used here, the generator has a high impedance, low voltage circuit that provides safety and the necessary high current density on the work coil. Now, the alternating magnetic field set up by the work coil (acting somewhat like the primary of a transformer) induces eddy currents on the sample (the secondary of the transformer) which tend to concentrate nearer the outer surface of the metal as the alternating current frequency increases. The natural resistance of the metal to the passage of current is the process by which heating occurs on the surface. Note then that a metal with a very low electrical resistivity as well as a non-metal with a high resistivity will be very difficult to heat using an induction heating system. Again, if the heating is done slowly enough, natural conduction from the surface will keep the sample at almost uniform internal temperature.

a. Apparatus Description

Since the complete induction furnace facility (See Fig. 8) was used by Mellor, a thorough description of its parts will be found in Ref. 12; however, the main components will be described here for the sake of completeness. Looking
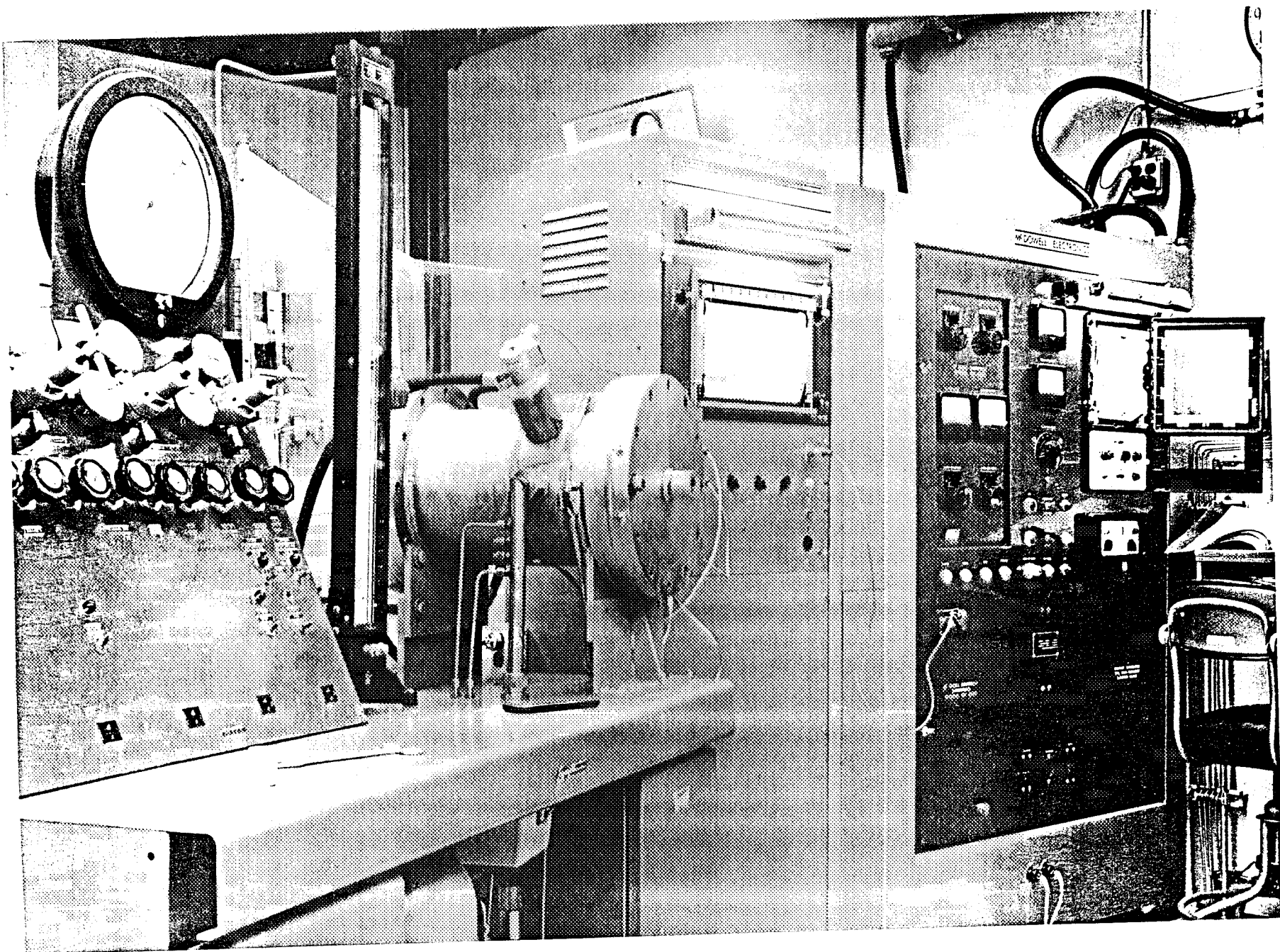
FIGURE 8

at Fig. 8, to the right of the photograph is the RF gen-
erator, at the center is the instrumentation rack, and to the
left is the control panel and the pressure vessel housing
the work coil. Each of these components will now be dis-
cussed separately.

The radio frequency generator, model 10KW-2DFCT/LA, was
build by McDowell Electronics, Inc. of Metuchen, New Jersey.
This model has two no load frequency ranges (0.5-0.7, 2.0-5.0
Mcycles/sec) and its output power is continuously variable
from 1.2 to 12 KW. It is equipped with a Leeds and Northrup
Speedomax H AZAR (adjustable zero, adjustable range) strip
chart potentiometric recorder and a Three Action Series 60
Control Unit which provides automatic temperature control spec-
ified to within $\pm 0.5^\circ C$ at any chosen preset temperature.

In this investigation, the Leeds & Northrup control
unit was used in conjunction with a differentiating circuit
(12) which provided instead for a control system that main-
tained a constant rate of change of temperature with time.
The differentiating circuit, housed in the instrumentation
rack, established automatic control of the heating process
at a specific preset value of the sample heating rate.

A schematic of the pressure vessel and its control
system is shown in Fig. 9. The cold trap, filled with liquid
nitrogen, serves to protect the vacuum pump from any metal
vapor entrained in the gas. The mixing chamber is used to
store gas mixtures of desired proportions until needed in
the test vessel. The dryer is a Matheson Co., model 460 Gas
Purifier used to dehumidify the gases before entrance into
the pressure chamber.

The steel test chamber is about 25 cm in diameter and
about 43 cm in length (21.3 l. in volume) and has a maximum
operating pressure of 20 atm. It is lined with a 1.6 mm

HR

OXIDIZER

HR

DILUENT

HV

MANOMETER   0-500PSI

TEST CHAMBER
1300 CU. IN.

QUARTZ
WINDOW I IN. DIA.

SAMPLE

WORK
COIL

HV

HV

HV

HV

HV

HV

SV

HV

DRYER

HV

HV

COLD TRAP

V

BD

PSI
TING

355 PSI
BURST PRESSURE

MIXING
CHAMBER
4100 CU. IN.

SV

VACUUM
PUMP
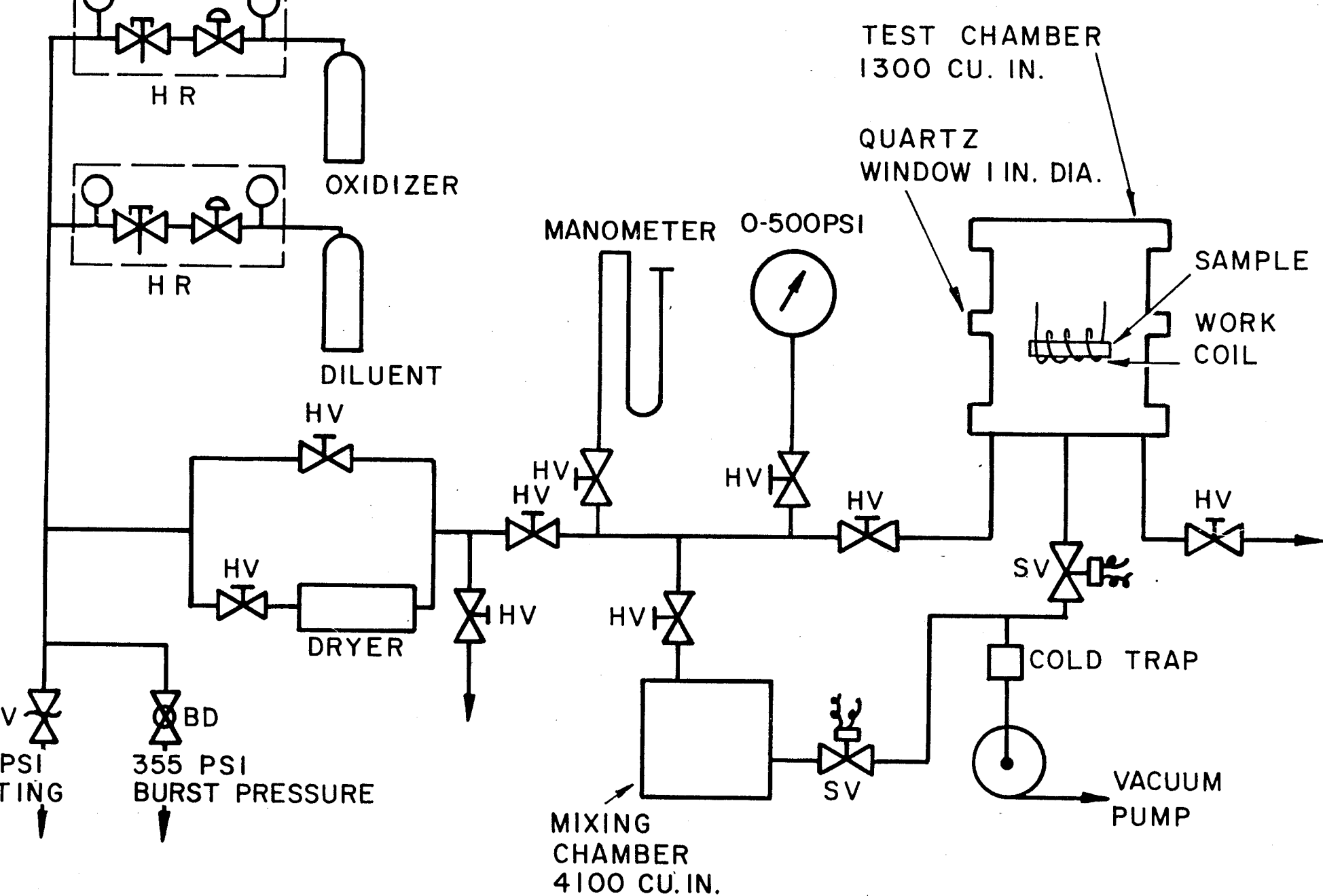
INDUCTION FURNACE FACILITY TEST APPARATUS SCHEMATIC

thick aluminum annulus to protect the chamber from hot metal
and to minimize electromagnetic coupling between the chamber
and the work coil. The outside of the chamber is water
cooled in order to prevent overheating.

The work coil is centered in the test vessel 15 cm
from the front door in line with two 2.54 cm diameter quartz
windows situated at the side of the vessel, 45° from the
vertical. In most of the experiments performed here, a $4\frac{1}{2}$ turn,
2 inch diameter work coil was used. This coil was made from
$\frac{1}{4}$" copper tubing, since high frequency current tends to travel
on the surface of any wire and water cooling is necessary for
even a metal of low resistivity such as copper. Visual ob-
servations were made through a neutral-density filter using
the above quartz windows along with two similar windows at
the center of the front and back plates.

Heating is accomplished, as shown schematically in
Fig. 10, by centering the metal sample within the work coil
via a suitable arrangement of fire bricks. A thermocouple
is mounted within the sample through a hole drilled into the
bottom of the crucible and is connected to the appropriate
lead wires within the chamber. The primary recording unit
for the thermocouple output voltage is a Model FS02W6L Servo/
Riter II Potentiometric Strip Chart Recorder built by Texas
Instruments, Inc.

b. Effective Induction Heating

It is important to digress here to consider the methods
available for increasing the performance of any induction
furnace. Here, performance is measured in terms of the
maximum sample temperature that can be attained for any par-
ticular metal, since induction furnaces are in general power

SCHEMATIC OF EXPERIMENTAL CONFIGURATION
FOR INDUCTION HEATING

TO RECORDER

THERMOCOUPLE

FIRE BRICK

WATER OUT

METAL SAMPLE

WATER IN

CRUCIBLE
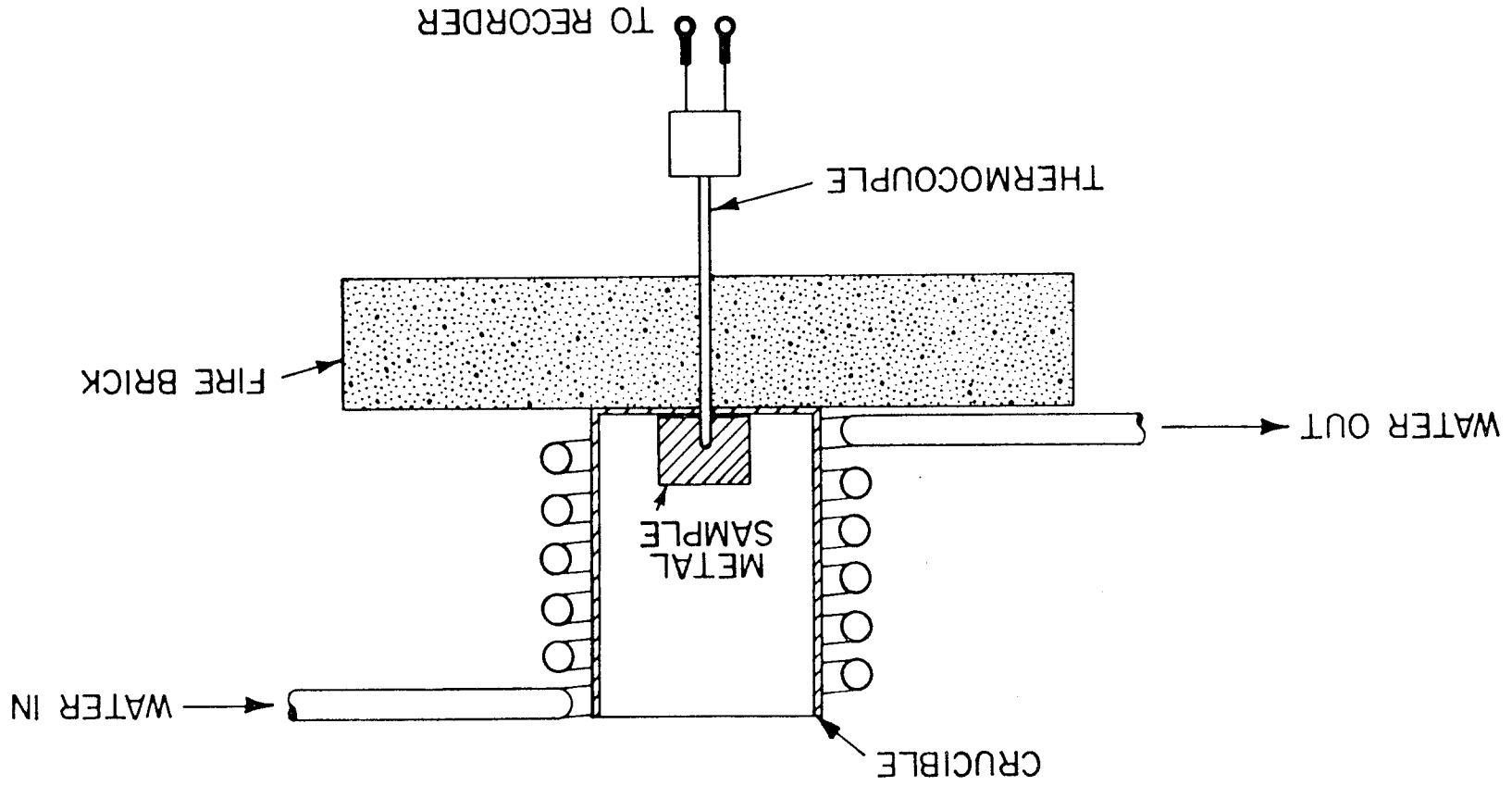
limited rather than temperature limited. Obviously the attainment of higher temperatures is critical in dealing with such metals as aluminum, which when heated in an oxygen atmosphere, has an ignition temperature greater than 2000°C.[1]

Effective induction heating is generally dependent on four variables: (1) The frequency of the power supply; (2) The design of the heating coil; (3) The power of the generator; (4) The resistivity of the metal sample. However, since the maximum power of the generator and the resistivity of the sample are fixed in any single experimental situation, only the first two of these can be controlled to any significant extent.

Most modern power supply units are capable of being applied at several different frequencies. Specifically, the particular generator used here has two separate circuits, one of which supplies current at frequencies four times that of the other. Since power input to the sample varies as the square root of the frequency (30,31), this means that higher frequencies would produce twice the power input to the sample in this case. Unfortunately, high frequencies in this range (2.0-5.0 Mcycles/sec) are not only more dangerous in operational use because of the possibility of high frequency burns, but also cause grave problems of proper insulation due to dielectric heating, and, even worse, cause frequent arcing due to a breakdown of the oxidizer gas in even moderately low pressure atmospheres.

Consequently, here, as in most other cases, it becomes necessary to rely almost completely on a well-designed coil

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[1] The interested experimentalist will find that Refs. 29-33 cover this subject matter quite well. Much of the information contained here is extrapolated from Ref. 30.

in order to improve the system and obtain optimum performance from the given power source. Indeed, this is the approach that was used in the present experimental investigation. Although the final results fell somewhat short of original expectations, enough significant improvement was made to show that coil design is perhaps the most important experimental parameter in induction heating. This is not terribly surprising when one realizes that the work coil is the sole means by which power is transferred from the generator to the sample. Thus, obviously, the coil geometry is responsible not only for the distribution of heat within a metal sample, but also for the magnitude of heat input needed, according to some pre-determined heating requirement.

Although there are some empirical mathematical formulae that indicate the geometry of a coil, they are only applicable in the simplest cases and will not be discussed in the present report (29). However, the principal results of these formulae, as shown much more conclusively through experience, are certainly of interest here. They show that the geometrical design of work coil best suited to give the most efficient heating is obtained by maximizing the coil current and providing the closest possible coil coupling with the work load.

Consider first the problem of optimizing the maximum current through the work coil. Although there are several rules here (30)[2], the most important terms of difficulty is to match the impedance of the work coil with that of the generator tank circuit coil. This is usually done by a trial and error technique because of the individual nature of each high frequency generator. Specifically, the generator used here provides a high impedance, low voltage, circuit which requires that the coil have a minimum of four turns and be within

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[2]These are mainly geometrical rules to avoid excess inductance losses, such as keeping all coil leads close together and maintaining the current flow in each segment of the coil in the same direction.

certain limiting diameters in order to be effective. As mentioned previously, in these experiments a $4\frac{1}{2}$ turn, 2" diameter coil was generally used; these dimensions were determined through a trial and error procedure that sought to maximize the sample temperature by choosing those dimensions that kept the work coil impedance matched over the entire power range of the generator. For some metals of higher conductivity, impedance matching was achieved by designing a more complicated work coil that consisted of two concentric coils, one inside the other, each of which had $4\frac{1}{2}$ turns, such that the interior coil had a 2" diameter and the exterior coil had a 4" diameter. This particular coil arrangement was also found to be extremely useful for achieving higher temperatures in the automatic control mode of the furnace for all metals of interest.

The other criterion for good coil design, close coil coupling, is essentially controlled by geometrical factors such as the height and diameter of the coil and the geometry of a single turn of copper tubing.[3] Most influential in the majority of cases is the diameter of the coil. At the frequencies used here, it is of importance to have the coil as close as possible to the load (32). Although uniformity of heating may be sacrificed, there is usually a substantial increase in the heat density at the metal surface and consequently, the sample temperature, when this approach is used.

Unfortunately, in contrast to melting point experiments, two important experimental problems arise in these investigations which severely limit the extent of coil coupling with

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[3] For example, it is known that better heat penetration is obtained if the copper tubing is somewhat flattened since this results in a higher current density on the surface of the coil facing the sample.

the metal sample. First, because of the relatively high frequencies used here, arcing becomes very troublesome when coupling is too close, especially at the lower pressures. Secondly, and more important, the fact that combustion does occur precludes any close coil coupling with the sample, since, especially for vapor-phase burning metals, the coil may become damaged thus allowing the circulating water to feed the metal fire and cause a serious fire hazard. In fact, even with the conservative coupling used in this investigation, at times the flowing water in the coil has instantaneously boiled due to this extreme heat transfer problem. Closer coupling will require that the coil be coated with an insulating lacquer of some type or be completely covered with a high temperature ceramic. Both of these approaches, which also help to alleviate the arcing problem, could prove very useful in future work.

2. The Aluminum Work--An Experimental Problem

Recall that it was originally decided to investigate the ignition of aluminum to ascertain the hypotheses that a transition temperature controlled metal has its ignition temperature independent of sample size. However, numerous attempts to ignite bulk aluminum samples proved unsuccessful due to several experimental difficulties which appear to be insurmountable at the present time. These experimental problems are mainly due to two properties of aluminum which are very critical for properly controlled induction heating: (1) Aluminum is a vapor-phase burning metal which also has a very high ignition temperature ($\sim 2040^{\circ}C$). (2) Aluminum is blessed with a very low electrical resistivity.

The above properties of aluminum were responsible for many attempts to optimize the induction furnace system, primarily through good coil design. Although the combustion

problem did not allow close coil coupling as is strongly needed in this case, the difficulties with aluminum did lead, via many trial and error procedures, to an optimum design for an unprotected coil which was used in all other experiments. This is the 4½ turn, 2" diameter coil discussed previously.[4]

Considering the high ignition temperature of aluminum and the fact that power input to the sample as transferred from the coil is minimized by highly conductive metal loads, it is no wonder that this metal could not be ignited. Moreover, crucibles that have desirable thermo-mechanical properties at these temperatures in a pure oxygen atmosphere are very difficult to find. Alundum (predominantly Al_2O_3) crucibles cannot be used since they obviously will melt as the aluminum metal ignites. Silicon Carbide (SiC) crucibles tend to break apart in an explosive fashion near 1500°C. Zirconium dioxide (ZrO_2) and, to a much lesser extent, Sili-Oxi-Nitrate (SiO_2N_2) crucibles hold together fairly well but at times tend to crack as heating progresses. Boron Nitride crucibles appear to give by far the best performance, but the usual loss of one crucible for each experimental run makes the cost of this item prohibitive.[5]

For a time, it was thought that using a conductive crucible would solve this problem since then the crucible could be heated directly and the sample heated by conduction and radiation from the crucible, thus circumventing the problem posed by the extremely low resistivity of aluminum. However, the only two practical conducting materials could not be used

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[4]This optimum coil connected to the low frequency side of the present generator gave maximum aluminum sample temperatures of near 1500°C.

[5]Nearly all crucibles were supplied by the Norton Company of Worcester, Mass. The boron nitride crucibles were supplied by Union Carbide.

since SiC crucibles broke apart thus short-circuiting the system as they made contact with the coil, and graphite crucibles could not be coated with any ceramic which would prevent complete oxidiation of the crucible in a pure oxygen atmosphere. In addition, this system would not allow pure surface heating, which emphasizes the pyrophoric behavior of metals, as required to indeed prove that aluminum has an ignition temperature independent of sample size.

In conclusion then, unless methods are found which allow higher frequencies, the present generator does not appear to provide enough power to overcome the high conductivity of a metal such as aluminum. There seems, however, to be one method to improvise the present system that might provide a solution. In high inductance systems, a series-resonance circuit typically gives rise to an extremely significant current increase at the cost of lowering the circuit impedance. Obviously, such an increase in coil current would lead to a greater power input to the metal sample. Moreover, these series-resonance circuits are reported to be extremely satisfactory in that highly conductive metals can be made to reach fairly high temperatures (30).

3. The Design of the Bulk Ignition Temperature Experiments

Upon the failure of the aluminum work, the second area of interest, that is the experimental compilation of ignition temperatures of other common non-toxic metals, became the major experimental problem and it is the results of this work that are treated in detail in Chapter IV.

The metals to be investigated were chosen such that they could be easily ignited in the bulk configuration using the previously described induction furnace. Any metal which did not ignite over the entire pressure range of interest (300 torr to 5 atm.) due to a high ignition temperature or

materials problems in handling such metals was immediately removed from further investigation. However, fragmentary data concerning such metals (cobalt, copper, titanium, tungsten, zirconium) are reported briefly in the next chapter.

In this investigation, only atmospheres of pure oxygen were used for several reasons. First Mellor (12) showed that variations in heating rate had the least effect on the ignition temperature of bulk samples in the case where oxygen was the ambient atmospheric gas. Second, Mellor (12) also showed that the greatest reproducibility in these types of experiments was obtained when oxygen was used as the atmospheric gas. Finally, in considering the future application of such data to developing more quantitative models, it appears that there is more known about low temperature oxidation reactions, heterogeneous reaction kinetics, and gas adsorption on metals for an atmosphere of pure oxygen than for any other gas.

Mellor (12) also showed that the effect of heating rate was nearly negligible in the regime of 10 to 200 $^{\circ}$C/min when ignition temperature experiments were being done in the bulk range in an oxygen atmosphere. Thus the present investigation was standardized to use a heating rate of 75°C/min for metals which ignited below approximately 1000°C and 150°C/min for metals which were thought to ignite above 1000°C.

Usually, three or more runs were made for each metal at each pressure of interest--300 torr, 1 atm., and 5 atm. The experiments were generally limited to 300 torr because of arcing problems and 5 atm. because of the explosive qualities of vapor-phase flames at higher pressures thus giving rise to the possibility of damage to the coil.

A chromel-alumel thermocouple was used in all runs for both temperature readings and automatic control of the furnace heating rate. This thermocouple was placed in the center

of the sample in order to avaoid inaccurate temperature
measurements in the surface zones where the eddy currents
are predominant. In general, if the thermocouple was placed
in good contact with the metal sample, it usually picked up
very little extraneous noise from the magnetic field pro-
duced by the work coil. Whenever possible, the thermocouple
was calibrated by measuring the sample freezing point and
comparing with the known metal melting point. As pointed out
by Mellor (12), this type of calibration includes all possible
sources of error such as induction heating of the thermo-
couple, lack of contact between thermocouple and sample,
and errors in recorder reading. In these investigations, the
average experimental error was on the order of 5 to $10^{\circ}C$.

a. Experimental Procedure

The metal sample to be ignited was cleaned and weighed.
It was placed in a crucible so that a hole drilled in the bottom
of the sample covered the thermocouple which extended through
a hole in the bottom of the crucible. The crucible and metal
were mounted in the center of the work coil using a suitable
arrangement of firebricks and the thermocouple was connected
to the appropriate lead wires.

Upon closing the front door of the chamber, the pres-
sure vessel and feed system were evacuated to a pressure on
the order of one torr. The chamber was then filled with
oxygen at the desired pressure directly from a gas cylinder.
The experimental run then began as the furnace was turned on.

As soon as ignition occurred, the furnace was turned
off and the pressure vessel was purged with high pressure
argon as the oxygen gas was exhausted. After the metal fire
was extinguished[6], the chamber was exhausted to 1 atm. and

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[6]This was done as quickly as possible to avoid damage to the
coil. This facility is not suitable under existing conditions
for the study of metal combustion.

opened so that the sample remains, crucible, and thermocouple could be removed.

b. Gases

Throughout the present investigation, only pure oxygen atmospheres were used and argon was used for all purging operations. For both these gases, commercially pure specimens were used; typical analyses of these gases which were obtained from the Liquid Carbonic Division of General Dynamics, are listed in Table 2.

TABLE 2

TYPICAL ANALYSES OF GASES

Oxygen: 99.5%

$N_2 + H_2$ <5000 ppm

H_2O <11 ppm

Argon: 99.998%

N_2 <10 ppm

O_2 <10 ppm

H_2O < 5 ppm

As indicated previously, static gas atmospheres of 300 torr, 1 atm (760 torr), and 5 atm (3800 torr) were used for all metals. The one exception was the extended investigation of the metal zinc where atmospheres of 200 torr, 3 atm (2280 torr), 7.5 atm (5700 torr), 10 atm (7600 torr), 12.5 atm (9500 torr), and 15 atm (11,400 torr) were also used. Thus in most cases, a pressure range of only one order of magnitude

was established, and it was therefore expected that a very large variation in ignition temperature would not occur.

c. Metals

All metals used in the present investigation were obtained in rod form from A. D. MacKay, Inc. of New York. Each metal was cut to size from the original rod so that the surface to volume ratio (S/V) was kept in the bulk range. Although the work of Mellor indicates a wide bulk range stretching from an S/V of 0.01 to 1.00 mm^{-1} in an oxygen atmosphere, most samples were cut so that $0.25 < S/V < 0.35$ mm^{-1} in order that the bulk ignition temperatures might be compared in a standard form.

The bottom of each cylindrical sample was drilled along its centerline until a hole 1/8" in diameter and 0.50 cm deep was obtained in order to house the thermocouple junction. The bottom edge of all samples was beveled slightly in order to assure that this surface was in contact with the crucible. Thus, for purposes of the S/V calculation, it was assumed that the bottom surface of the sample was not exposed to the oxidizing gas, and that the reaction surface then consisted of the side and top surface of the cylindrical metal specimen. This geometrical surface area was assumed for all metals, even for those in which the sample melted before ignition; therefore, in all cases, a room temperature value of S/V was used.

Table 3 lists alphabetically all the metals used in the present investigation, along with their purity, geometrical dimensions, and surface to volume ratio (S/V). These figures represent the average values for all samples of any particular metal. For the sake of convenience, those five metals which were used very sparingly are also included at the end of the list. For all metals, the surface area of

the sample was calculated as indicated above from the average geometrical dimensions. The volume was calculated from the average mass of the samples of any particular metal and the room temperature density of that metal. From these, the S/V was easily computed.

TABLE 3

SAMPLE DIMENSIONS OF EXPERIMENTAL METALS

Metal	Purity (%)	Diameter (cm)	Length (cm)	S/V (mm^{-1})
Ba	99.99	2.14	1.83	0.239
Bi	99.999	1.23	2.57	0.365
Ca	99.5	2.37	1.0	0.365
Fe	99.9	2.52	1.0	0.264
Pb	99.999	1.27	2.60	0.357
Mg	99.96	2.38	1.0	0.285
Mo	99.95	1.59	2.06	0.306
Sr	99.0	1.64	1.75	0.309
Sn	99.999	1.24	2.58	0.366
Zn	99.9	1.90	1.71	0.277
Co	99.5	1.02	1.97	0.456
Cu	99.95	1.91	1.54	0.281
Ti	99.5	2.54	1.0	0.261
W	99.9	1.90	–	–
Zr	99.95	1.50	2.52	0.303

Before all runs, most metal samples were washed in hexane and allowed to dry and degas in a room temperature environment for 24 hrs. Exceptions were bismuth and lead which are somewhat toxic, and the three metals, barium, calcium, and

strontium, which oxidize quickly at room temperatures. These latter three metals were shipped, stored, and machined under mineral oil. In early experiments, they were washed in hexane for one hour at room temperature, and then degassed in a vacuum desocator (with continuous pumping) for at least 24 hrs. In later experiments, each sample was put into a vapor degreaser using liquid freon for approximately three minutes just prior to the experimental run. This method visually appeared to give much better results and also provided very little time for sample oxidation as in the previous method.

d. Auxiliary Materials

Throughout all these experiments, a chromel-alumel thermocouple with an ice bath reference junction was used. The thermocouple wire leads were protected with 1/8" double bore ceramic tubing constructed from Alundum. All the crucibles used in this particular investigation were also made from Alundum and were obtained from the Norton Company of Worcester, Mass. For all metals investigated here, the above materials were satisfactory as long as the metal fire which ensued after ignition was promptly extinguished.

The firebricks upon which the sample crucibles rested were Type HW-30LI insulating firebricks, adequate up to about $1500^{O}C$. They were supplied by the Harbison-Walker Refractories Company, Pittsburgh.

CHAPTER IV: THE BULK IGNITION TEMPERATURE INVESTIGATION: RESULTS AND
          DISCUSSION

As outlined in the last chapter, the failure of the
proposed aluminum work led to a more general investigation
of the bulk ignition temperature of ten common metals, along
with a preliminary investigation of five others. The prime
purpose of these experiments was to provide essential
information needed as background material for the anticipated
future development of a more cogent quantitative model of
heterogeneous metal ignition. This information consists of
not only the raw data, i. e., the actual measured ignition
temperatures, but also deductions extrapolated from these raw
data that can contribute to a fuller understanding of the
overall ignition phenomenon. These extrapolations are of
great necessity in dealing with some of the basic problems
of metal ignition, such as developing suitable methods for
determining critical temperatures and investigating more
deeply the very interesting question of metal pyrophoricity.
In addition, the measured ignition temperatures can be of
great use in various engineering applications related to
rocket performance, such as, for example, metal ignition
augmentation, i. e., the process of coating hard to ignite
metals such as aluminum with other metals which can signifi-
cantly lower the ignition temperature of the conglomerate
particle.

Since no quantitative model yet exists which can
correlate to any degree the ignition temperatures measured
in the present investigation (See Section 2 of this chapter),
one of the more important future applications of these
data cannot be discussed in this report. However, as will
be brought out in this chapter, there are at least two very
important concepts indigeneous to this investigation that
could lead to a better experimental and theoretical under-

standing of the chemical and physical processes which control the ignition phenomena. First, there is evidence to show that transition temperature controlled metals, such as aluminum, could be ignited at much lower temperatures at low ambient pressures due to a decrease in the metal boiling point which appears to control the transition temperature at these pressures. Second, the overall results indicate that a bulk ignition temperature can be consistently defined for metals in an oxygen atmosphere despite changes in the heating environment.

In addition: (1) The variation of ignition temperature with pressure may be the result of whether a particular metal is critical or transition temperature controlled. (2) A visual and interpretive study of the ignition process indicates that some empirical rules could be established that put limitations on the metal ignition temperature. These types of rules could eventually help to differentiate between the ignition of metals which burn on the surface and those that burn in the vapor phase.

In order that the present results may be discussed, it is necessary to list here the fundamental temperatures of interest for those metals used in the present investigation. These include the melting and boiling points of the metal and predominant metal oxide, both for the ten principal metals of interest in this investigation and those five metals for which fragmentary data were obtained. Also included in Table 4 is the estimated transition temperature for these metals. This information was obtained primarily from Ref. 21, but Refs. 12, 23, and 24 were also used in order to list the most consistent and best possible values for the transition temperature. The melting and boiling points were taken from Refs. 21, 28, 34, and 35 with Ref. 34 as the major source of information.

1. The Variation of the Transition Temperature
a. Previous Results with Aluminum

Recall that in the early work with aluminum, Brzustowski (4,9) found,

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TABLE 4
FUNDAMENTAL TEMPERATURES OF INTEREST FOR METALS*

Metal	Metal Oxide	Metal Melting Point	Metal Oxide Melting Point	Metal Boiling Point	Metal Oxide Boiling Point	Transition Temperature
Ba	BaO	710	1923	1527	2000	<17
Bi	Bi_2O_3	271	860	1470	1890	-
Ca	CaO	848	2580	1240	2850	400
Fe	FeO	1536	1420	2872	-	>1200
Pb	PbO	328	897	1753	1516	550
Mg	MgO	650	2800	1105	3600	450
Mo	MoO_3	2620	795	4507	1155	700
Sr	SrO	774	2430	1366	3000	-
Sn	SnO_2	232	1127	2260	1850	475
Zn	ZnO	419	1975	907	-	>700
Co	CoO	1495	1935	3550	-	>1350
Cu	Cu_2O	1083	1235	2595	-	>1000
Ti	TiO_2	1677	1855	3277	2750	850
W	WO_2	3410	1580	5900	-	~1000
Zr	ZrO_2	1855	2677	4474	4300	≥1300

*Taken and extrapolated from Refs. 12, 21, 23, 24, 28, 34, 35; given in °C. Boiling points are for atmospheric pressure (760 torr)

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as had other investigators, that the ignition temperature of this metal in oxygen-argon atmospheres was very close to the melting point of its oxide. Brzustowski also noted, however, that the brightness temperature at ignition for anodized aluminum wires, though constant from 20 atm. to 1 atm., slowly decreased from total pressures of 300 torr

to 50 torr. Although Brzustowski (4) attributed this be-
havior to a change in emissivity, it is very possible that
the ignition temperature of aluminum decreases with decreasing
oxidizer pressure at these lower ambient pressures. Indeed,
Kuehl (14) later found that, whereas the ignition temperature
of aluminum is constant at the oxide melting point at higher
pressures, for pressures lower than approximately 250 torr,
the ignition temperature slowly decreases with decreasing
ambient pressure.

Since aluminum is transition temperature controlled,
the above behavior of its ignition temperature may logically
be explained via some mechanism that would allow the transi-
tion temperature to decrease with decreasing pressure below
300 torr. Such a mechanism has been proposed by Kuehl (14)
and is depicted on the pressure vs temperature plot in Fig.
11.

The normal transition temperature for aluminum is
known to be its metal oxide melting point, 2042°C. This is
represented by the straight vertical line in Fig. 11. Con-
sider now the vapor pressure curve for aluminum metal; from
Fig. 11, it can be seen that the oxide melting point is
equal to the metal boiling point at a pressure of about
700 torr. Thus at pressures above 700 torr, the pressure of
the aluminum vapor enclosed by the oxide coating can never
exceed the total ambient pressure without having the temper-
ature of the sample become greater than the melting point of
Al_2O_3. Therefore, at pressures greater than 700 torr, the
transition (and ignition) temperature of aluminum is pos-
tulated to be the melting point of the metal oxide.

For ambient pressures below 700 torr, the vapor pres-
sure of aluminum inside the solid oxide shell will become

MELTING POINT OF Al_2O_3

VAPOR PRESSURE
OF ALUMINUM

T_{trans} FOR A WEAK OXIDE SHELL

T_{trans} FOR A STRONG OXIDE SHELL

P (Torr)

700

250

2042

T (°c)
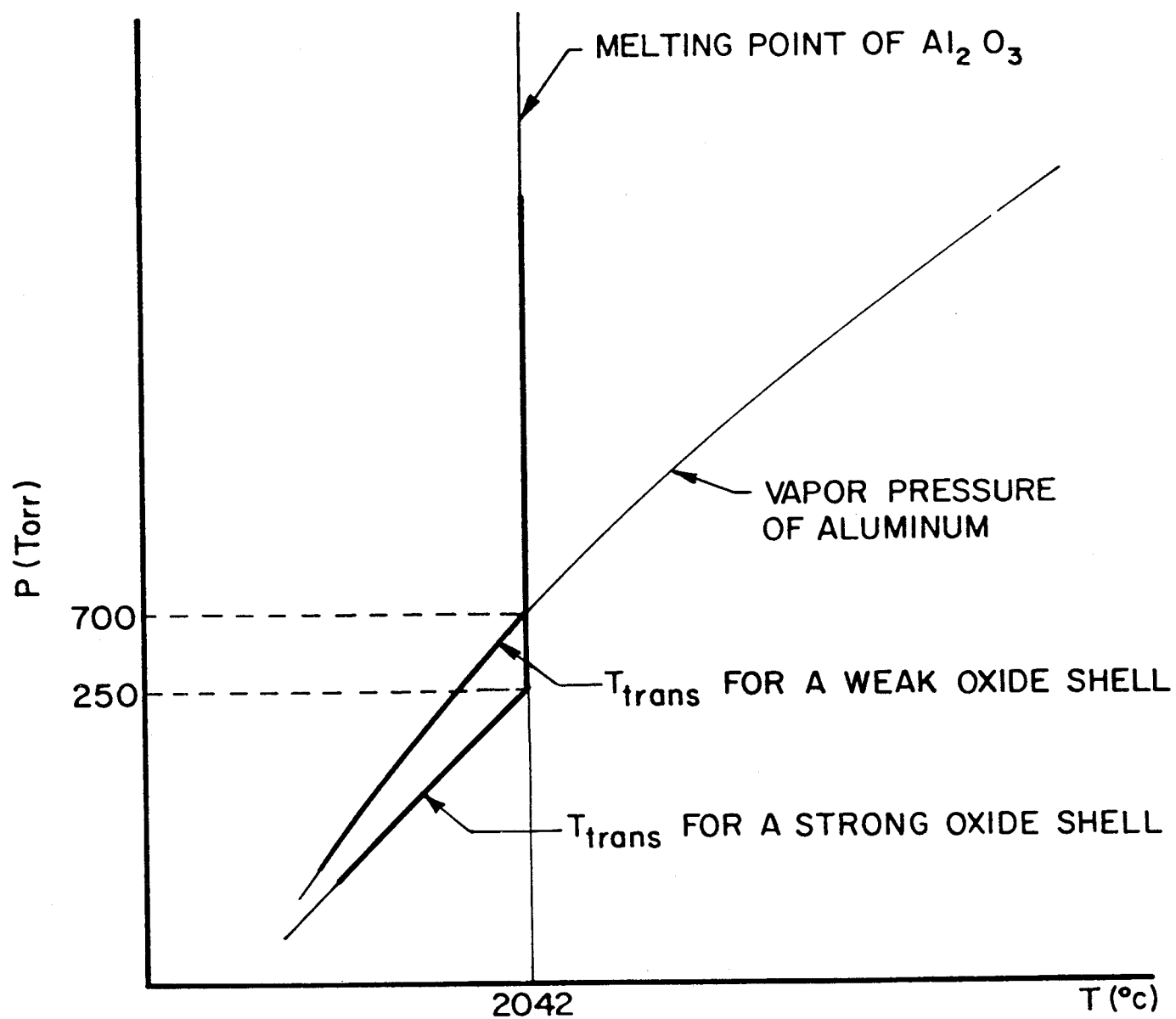
TRANSITION TEMPERATURE VS
PRESSURE FOR ALUMINUM

FIGURE II

larger than the outside ambient pressure for temperatures greater than the appropriate boiling point of aluminum at the pressure of interest. Thus, it is not possible in this pressure range to reach the oxide melting point without causing a pressure differential across the oxide shell. Depending on the strength of the oxide layer then, it is possible that a certain pressure differential may break the oxide coating at temperatures below the melting point of Al_2O_3. If the oxide coating is thin and weak, but impervious to the ambient oxidizer, then the transition (and ignition) temperature below 700 torr will closely follow the vapor pressure curve. On the other hand, if the oxide coating is thick, strong, and protective, as is usually the case with aluminum, a higher than ambient metal vapor pressure will be needed to break the oxide coating. Therefore the transition temperature for pressures below 700 torr will follow a path similar to that found by Kuehl (14) as depicted by the lower curve in Fig. 11.[1] (Note that a pressure drop from 700 to 250 torr is needed in the case of aluminum to have a large enough pressure differential to break the oxide coat.)

In summary then, the ignition temperature for aluminum is postulated to be controlled by the oxide melting point at higher pressures and the metal boiling point at lower pressures. However, aluminum still remains completely transition temperature controlled since the metal boiling point, like the oxide melting point, is a physical property of the metal-oxidizer system and not a chemical property, dependent on the heating characteristics of the system. Thus, it is concluded that the transition temperature may vary considerably with pressure when the metal boiling point interferes

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[1] Notice that the lower curve approaches the vapor pressure curve at very low pressures. This is to be expected since at very low pressures, the oxide shell naturally becomes thin and weak. The heavy lines in Fig. 11 denote the transition temperature variation for both a strong and weak oxide shell.

with the natural melting process of the oxide.

Adding even more credance to this argument is the fact that it can be used to explain the cylindrical vapor-phase flame that appears upon ignition of aluminum wires in carbon dioxide-argon atmospheres at pressures below 300 torr (14). Recall that in Chapter I, this type of flame was explained by arguing that a barrier layer of Al_2O_3 exists which melts before the porous _outer_ layer of oxide, thus enabling metal vapor to escape before the wire breaks. Although this process may have a part in establishing the vapor-phase flame, the following argument seems to explain the observed phenomenon much more appropriately.

In heating the wire, the pores in the outer layer are only slightly filled by the pre-ignition oxidation process when the atmosphere contains CO_2-Ar mixtures. At ambient pressures above 300 torr, the oxide coat must melt before ignition can occur and hence a cylindrical vapor-phase flame does not appear. However, at pressures less than 300 torr (in agreement with Fig. 11), there exists a large enough pressure differential across the oxide shell to break the coating at its weakest points, specifically, near large pores, and thus allow metal vapor to escape without completely destroying the integrity of the oxide coat and hence the anodized aluminum wire. Consequently, it is indeed possible to observe the cylindrical vapor-phase diffusion flame at these lower pressures.

b. The Investigation of Zinc

Although the boiling point effect as described above seems to bring together and explain various results with aluminum, only Kuehl (14), using pyrometric means, has offered any evidence at all that indeed the ignition temperature of

aluminum at low pressures is controlled by a variable transition temperature which is in turn controlled by the metal boiling point. The fact that the ignition temperature of aluminum may be significantly reduced by using low pressures could be very useful in rocket applications. Therefore, it appears to be very important to determine if this phenomenon really does occur for metals such as aluminum.

Unfortunately, direct temperature measurements of bulk aluminum in the induction furnace was obviously not possible because of the reasons outlined in Chapter III. Consequently, it was thought that perhaps some other metal might be found which would also demonstrate this behavior at lower pressures. By using existing data on ignition temperatures and boiling points, it was thought that zinc might perhaps be transition temperature controlled due to a protective oxide layer, and that at lower pressures, its ignition temperature would be controlled by its boiling point. Data obtained using the induction furnace facility appear to bear out these original suppositions.

Table 5 lists the measured ignition temperatures of zinc to the nearest five degrees. In order to demonstrate the boiling point phenomenon, it was necessary to extend the pressure range beyond the 300 torr to 5 atm. regime used for all other metals considered in this investigation. As many runs as necessary were made at each pressure to assure consistency in the data. Note that at 300 torr and 5 atm, the ignition temperatures are divided into two ranges of data; the average of the lower range of data in terms of temperature is given by that average ignition temperature enclosed in parentheses. The reason for this division in data will be discussed shortly.

TABLE 5

IGNITION TEMPERATURES FOR ZINC METAL

Pressure	Ignition Temperature ($^\circ$C)	Average Ignition Temperature ($^\circ$C)
200 torr	785	790$\pm$5
	795	
300 torr	815	840$\pm$30
	835	(830$\pm$15)
	840	
	880	
1 atm	895	905$\pm$15
	905	
	920	
3 atm	1035	1040$\pm$5
	1040	
	1045	
5 atm	1090	1135$\pm$35
	1095	(1095$\pm$5)
	1140	
	1150	
	1160	
	1165	
7.5 atm	1160	1165$\pm$5
	1170	
10 atm	1140	1160$\pm$20
	1175	
12.5 atm	1185	-
15 atm	1290	-

In order to ascertain the validity of the boiling point effect, it is necessary to compare the average ignition temperature at each pressure to the boiling point of zinc at these pressures. The vapor pressure curve for zinc metal, as taken and extrapolated from Refs. 28, 35 and 36, is shown in Fig. 12. Note the near perfect correlation of the average ignition temperature at each pressure up to 7.5 atm with the boiling point of zinc. This indicates that zinc oxide is in all probability a protective oxide, but that it is thin and

IGNITION TEMPERATURES vs BOILING POINTS FOR ZINC

atm

10   75   5   3   1

PRESSURE (TORR)

10000 9000 8000 7000 6000 5000 4000 3000 2000 1000

TEMPERATURE (°C)
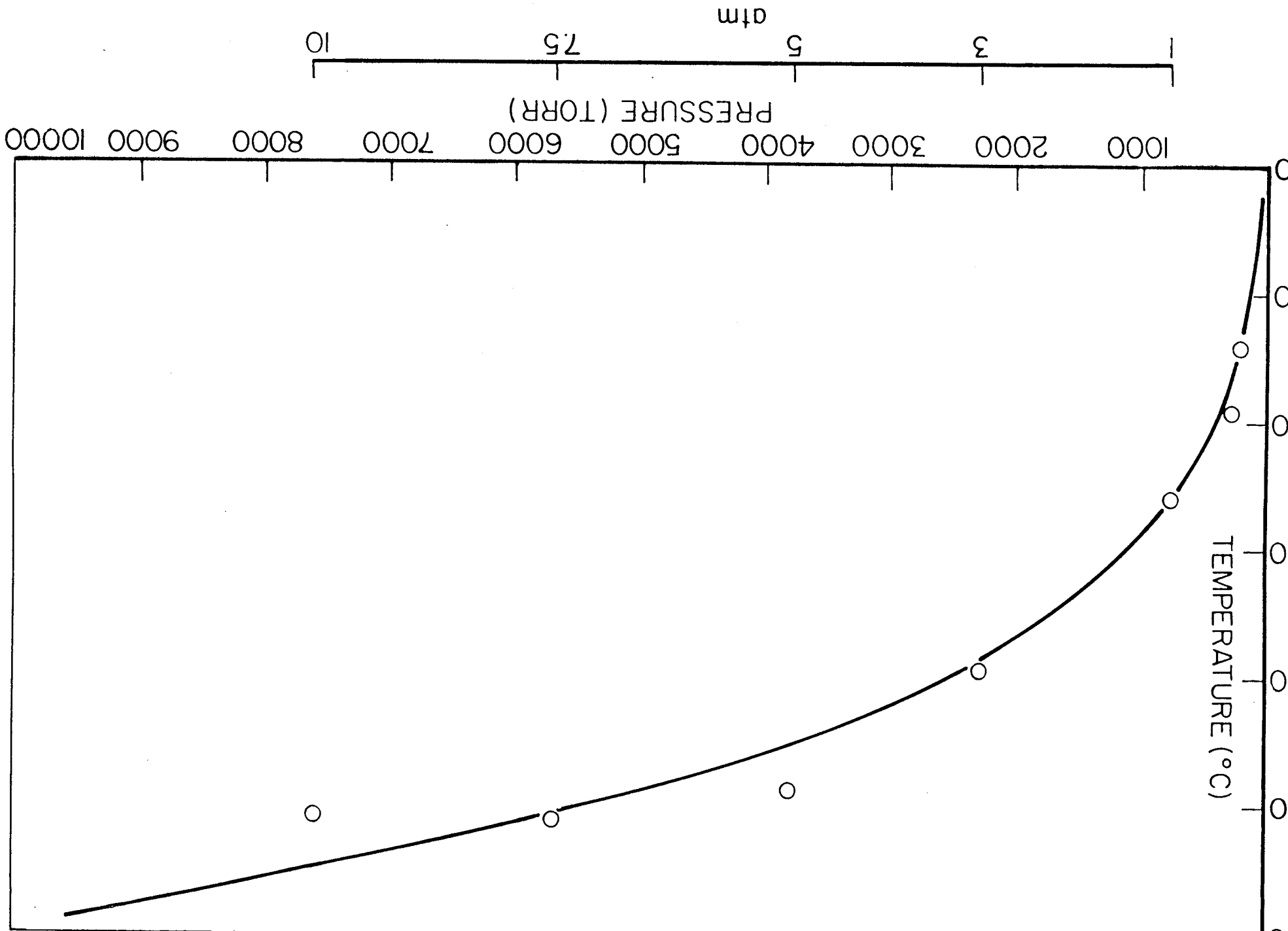
weak, and therefore only a slight pressure differential is needed to break the oxide shell. In order to see this point better, it is of interest to look closer at the data listed in Table 5.

At the lower pressures, especially at 200 torr, 1 atm, and 3 atm, there is almost perfect correlation with the zinc boiling point (At 760 torr, Table 4 gives $907^{\circ}C$ as the boiling point of zinc, for example). However, at 300 torr, there is a first indication that the oxide coat may at times require a sizeable pressure differential before it will crack. Nevertheless, in most cases at this pressure, the ignition temperature closely follows the vapor pressure curve as can be seen by comparing the average of the three lower experimental points (the average ignition temperature in parentheses) to the boiling point of zinc at 300 torr. A similar behavior is noted at 5 atm, but here the majority of the data points indicates that a higher pressure gives rise to a stronger oxide coat that, in general, remains protective until $1150^{\circ}C$. When, for some reason, a certain oxide shell is unprotective at this pressure, an ignition temperature comparable to the zinc boiling point at 5 atm ($\sim 1100^{\circ}C$) is obtained.

For those runs at 300 torr and 5 atm where the oxide shell is protective to a higher temperature than the corresponding metal boiling point, zinc metal scraps are usually found attached to the sides of the pressure vessel after the run has been completed. This indicates that the ignition process here was "explosive" in the sense that the large pressure differential across the oxide shell caused a spewing out of zinc metal upon breaking of the oxide coating just before ignition occurred. In addition, the temperature

traces for these particular runs show that immediately upon ignition, the molten zinc metal almost instantaneously drops in temperature to the appropriate metal boiling point. These particular experimental findings again seem to indicate that the zinc oxide shell is indeed protective to fairly high temperatures.

At higher pressures, the reaction is of course very rapid and at times, the metal is almost completely consumed before the metal fire can be extinguished. At both 7.5 and 10 atm, the ignition temperature is near $1160^{\circ}C$. This corresponds to the zinc boiling point at 7.5 atm, but to a temperature lower than the metal boiling point at 10 atm. It appears then that the protective qualities of the oxide coat are experimentally beginning to level off near $1150^{\circ}C$. Thermal oxidation data indicates that the zinc transition temperature is greater than $700^{\circ}C$; the present results increase the maximum value of the transition temperature to $1150^{\circ}C$ or perhaps higher. This, however, is still significantly less than the melting point of ZnO at $1975^{\circ}C$ (See Table 4).

The experimental data at 12.5 and 15 atm are not plotted in Fig. 12 because there is some doubt as to the significance of these results. At both of these pressures, the reaction is almost instantaneous and very explosive in the sense described above. At 15 atm, there was a sudden flash of light and no more; however, reaction had occurred since there was a thick layer of zinc oxide particles covering the entire inner surface of the pressure vessel. At 12.5 atm, there was no flash, but the furnace automatically shut down when the metal explosion occurred due to a short ciruit across the work coil caused by the flying zinc metal. (This also happened at 15 atm.) After a few seconds, light appeared from the remaining portion of the sample and reaction then proceeded.

Because of the extremely vigorous reaction and the imminent danger that it posed to the work coil, only one run was made at each of these pressures. However, even these very scanty data perhaps indicate that at higher pressures, the oxide coat becomes much thicker , leading to either the possibility of early cracking of the oxide layer or the presence of an extremely strong oxide shell which causes the transition temperature to increase with increasing pressure. The above statement however is to be considered very hypothetical in light of the lack of data supporting it.[2]

c.   Summary

The experimental investigation of the ignition temperatures of bulk zinc shows that, in general, the ignition temperature of zinc increases with increasing pressure in almost perfect correlation with its boiling point at the respective pressures involved. Because the ignition temperature may be greater than the metal boiling point, and the range of ignition temperatures is very large, it would appear that the oxide is protective to some high temperature, although not to the oxide melting point as for aluminum.[3] Indeed the maximum transition temperature, over the observable pressure range investigated here, appears to be near $1150^{\circ}C$, much less than the maximum _possible_ transition temperature for zinc at the melting point of ZnO ($1975^{\circ}C$).

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[2] In fact, due to the explosive nature of these reactions, it may be possible that the Al_2O_3 crucible perhaps acted as a catalytic agent or even entered into the reaction. There is however, no evidence for or against this hypothesis.

[3] If this were true, the ignition temperature would continue to rise until the ambient pressure increased over 260 atm at which pressure, the boiling point is equal to the melting point of the oxide ($1975^{\circ}C$). This is highly unlikely based on the high pressure results obtained in the present investigation.

This maximum transition temperature (1150^OC) denotes the end of the control of T_{trans} by the boiling point and the beginning of the control of T_{trans} by the physical characteristics of the zinc oxide coat as determined by the low temperature oxidation process prevalent in all metals.

Assuming that 1150^OC is indeed the maximum transition temperature for zinc[4], then below the vapor pressure at 1150^OC (7.5 atm), the boiling point of zinc will control the transition and thus the ignition temperatures (See Fig. 13 which conveniently depicts the data in Fig. 12 on a log P vs 1/T plot). However, the oxide coat for zinc, although impervious, is thin and weak; therefore, the ignition temperature will follow the vapor pressure curve instead of a curve similar to the lower curve for aluminum below 700 torr as depicted in Fig. 11. At very low pressures, both aluminum and zinc will follow their vapor pressure curves since very little oxidation takes place at these pressures and thus the aluminum oxide coat also becomes thin and weak. At pressures above 7.5 atm, the ignition and transition temperatures are here assumed to be constant at near 1150^OC.

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[4]Any other assumption for the maximum transition temperature will not change the reasoning in the argument outlined here. Thus 1150^OC corresponds to the melting point of Al_2O_3 at 2042^OC shown in Fig. 11. However, 1150^OC is not the melting point of ZnO, but instead represents the simple physical failure of the oxide layer to protect the metal substrate This phenomenon, as for all other metals, is characterized and defined by the transition temperature.
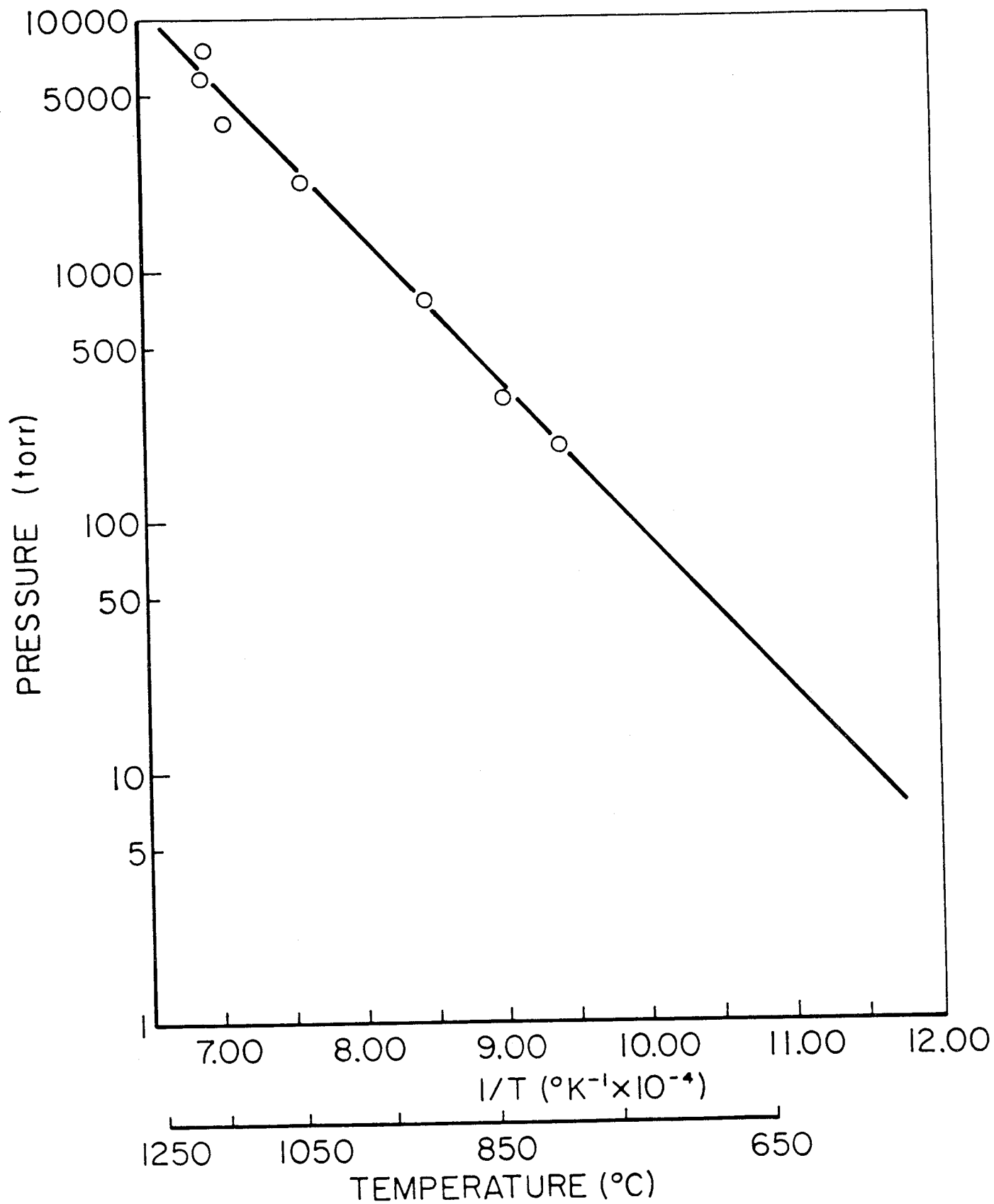
IGNITION TEMPERATURE VS BOILING POINT FOR ZINC

FIGURE 13

The overall results of the zinc investigation shows then that a transition temperature controlled metal can have its ignition temperature controlled by its boiling point for a certain range of low pressures. Thus for metals like zinc and aluminum, the transition temperature is not necessarily a constant but may be a strong function of pressure if the boiling point becomes the controlling influence in the ignition process. Consequently, although not common to most metals, the boiling point effect is indeed a proven influencing factor that very clearly explains the previously observed lowering of the ignition temperature and the cylindrical vapor-phase diffusion flame below 300 torr in early experimental work with aluminum metal.

2. The Consistency of the Bulk Ignition Temperature

a. The Experimental Results

Table 6 lists in alphabetical order those metals for which complete experimental data at pressures of 300 torr, 1 atm, and 5 atm were obtained in the present investigation. All ignition temperatures, based on melting point calibrations, were considered to be accurate to within 5 degrees and are so tabulated. The range of the experimental ignition temperatures for each metal at each pressures is readily available by referring to the third column of Table 6. Also calculated is an average ignition temperature at each pressure; however, it is realized that this particular temperature, especially for metals such as barium and strontium, which have a very wide range of experimental data at some pressures of interest, is not necessarily indicative of the true metal ignition temperature.

In light of the unknown effects of many environmental factors upon the metal ignition temperature, an average ignition temperature with a consistency indicated by a $25^{\circ}C$

TABLE 6

METAL BULK IGNITION TEMPERATURES

Metal	Pressure	Ignition Temperatures ($^{\circ}$C)	Average Ign. Temp. ($^{\circ}$C)
Ba	300 torr	550,560,620,630	590±45
	1 atm	480,510,570,650	550±90
	5 atm	535,540,600	560±30
Bi	300 torr	780,805,810,825	805±25
	1 atm	715,735,750,750	735±20
	5 atm	715,735,760	735±25
Ca	300 torr	790,795,800,800	795±5
	1 atm	785,785,805	790±10
	5 atm	760,775,805	780±20
Fe	300 torr	1310,1320,1330	1320±10
	1 atm	1300,1310,1340	1315±20
	5 atm	1285,1300,1315	1300±15
Pb	300 torr	845,850,860	850±5
	1 atm	845,855,860	850±5
	5 atm	810,830,840	825±15
Mg	300 torr	630,635,635	635±5
	1 atm	630,640,640	635±5
	5 atm	620,620,620	620
Mo	300 torr	795,795,810,810	800±10
	1 atm	780,785,785	780±5
	5 atm	740,765,765,785	765±25
Sr	300 torr	985,1015,1160	1055±85
	1 atm	935,1115,1175	1075±120
	5 atm	1125,1150,1165	1150±20
Sn	300 torr	975,1005,1015	1000±20
	1 atm	910,945,965	940±25
	5 atm	910,955,990,1000	965±45
Zn	300 torr	815,835,840,880	840±30
	1 atm	895,905,920	905±15
	5 atm	1090,1140,1150,1165	1135±35

range on either side of this computed temperature is considered to be a very desirable result. Obviously, an average ignition temperature with at least this amount of consistency gives a very good indication of the actual ignition temperature of the relevant metal at the pressure under consideration.

b. Comparison of Bulk Ignition Temperatures

Recall that in the original model of heterogeneous metal ignition, it was postulated that a consistent bulk ignition temperature could be defined. However, after lengthy experimental investigation, Mellor (12) stated that the transition temperature is the only consistent temperature that is of interest in metal ignition; the bulk ignition temperature is not consistent, but depends strongly on the experimental environment.

The previous section of this chapter has shown that the transition temperature may not be as constant as the above statement implies (It remains however a fairly stable indicator of the lower range of ignition temperatures). Moreover, in opposition to the restrictions imposed by Mellor's statement concerning the bulk ignition temperature, this section will attempt to demonstrate the following very important experimental conclusion: In at least a pure oxygen atmosphere, a fairly consistent bulk ignition temperature may be defined for each metal of interest, if the environmental conditions for the experimental determination of this ignition temperature are known. In order to show this, it is necessary to compare the results of the present investigation with the results of other experiments using a different igniting technique--in particular, resistance heating.

The bulk ignition temperatures of the metals of interest at 1 atm are compared in Table 7. The third column of this table lists the main basis of comparison in this

TABLE 7

COMPARISON OF BULK IGNITION TEMPERATURES

tal	Present Investigation	Grosse & Conway Results	Metal Melting Point	Metal Oxide Melting Point	Transition Temperature	Other Results
a	550 ± 90	175	710	1923	<17	
i	735 ± 20	775	271	860	-	805(12)
a	790 ± 10	550	848	2580	400	704-743(22)
e	1315 ± 20	930	1536	1420	>1200	
o	850 ± 5	870	328	897	550	
g	635 ± 5	623	650	2800	450	640(12)
o	780 ± 5	750	2620	795	700	623-630(37)
r	1075 ± 120	720	774	2430	-	
n	940 ± 25	865	232	1127	475	
n	905 ± 15	900	419	1975	>700	

development, i. e., the results obtained by Grosse and Conway (38, 39) using a resistance furnace at an ambient gas pressure of one atmosphere.[5] However, the metals in this case were heated in an _inert_ gas atmosphere to a certain temperature, and then exposed to oxygen which was slowly passed over the sample. Thus, in most cases, only a very thin and perhaps non-protective oxide layer was instantaneously built up on the metal before ignition could take place. This means that the "ignition temperature" recorded in this type of experiment may be closer to the critical temperature for the system. In addition, for those metals which have impervious oxides, one might expect that the "ignition temperatures" obtained by Grosse & Conway would be somewhat less than those obtained in the present experimental investigation in which a hindering oxide coat is allowed to grow on the metal surface.[6]

The last column of Table 7 lists the ignition temperatures of still other investigators who used bulk metal samples. These results, as in the present work, were obtained by heating the metal sample in an oxidizing atmosphere. As is easily seen, there is very little additional information of this type available in the literature. Thus, the present work remains as the only rather complete investigation of the ignition temperature of metals heated in an _oxygen_ atmosphere.

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[5]These results are, in general, considered accurate to $\pm 25^{\circ}C$ by the authors.

[6]Obviously, if such data were available, it would be much more advantageous to compare the present results with ignition temperatures obtained in a resistance furnace in which oxygen was used as the heating atmosphere.

Also included in Table 7 are the metal and metal oxide melting points and the estimated transition temperatures. These are taken directly from Table 4 and are repeated here for purposes of completeness and comparison. The boiling points of the metals are not included in this table since they are essentially irrelevant for the purposes of the present discussion. Comparison of the ignition temperatures from the present investigation (Table 7) with the metal boiling points listed in Table 4 and a study of the variation of these ignition temperatures with pressure (See Table 6) show that of these metals, only zinc has the property of having its ignition temperature in any way controlled by the appropriate metal boiling point. Hence, in most cases, the boiling point of the metal does not seem to be of prime importance in determining the actual value of any experimental ignition temperature.

Now, the data on the ignition temperatures of various metals, as found in this investigation, are of prime importance simply due to the fact that such data have for the first time been systematically obtained for a large group of metals heated at various pressures in a pure oxygen atmosphere. In addition, if these bulk ignition temperatures are consistent over some reasonably wide range of environmental conditions, the present data can easily be used for purposes of adequately predicting the ignition temperature of any particular metal. However, the ignition temperatures obtained in the present investigation, although generally very consistent from run to run, may not always be in agreement with other measurements made in a resistance furnace,

where (1) surface heating is not stressed, (2) heating is
generally slow, and (3) the environment is at the same tem-
perature as the sample. Therefore, in order to show that the
bulk ignition temperature is indeed consistent, Table 7
primarily compares the present results with those of Grosse
& Conway.

Consider first those metals for which the ignition tem-
peratures from these two investigations are, within experimen-
tal error, the same. These metals include bismuth, lead,
magnesium, molybedenum, and zinc. The above materials, ex-
cluding zinc, have a very thin oxide coat that appears to
become non-protective at fairly low temperatures due to several
factors. First, four of the above five metals have very low
metal melting points. The melting process tends to weaken the
oxide coating during the heating cycle prior to ignition.
Second, all of these metals have a fairly low transition tem-
perature. This either allows oxygen to reach the metal sub-
strate or controls the breaking of the oxide shell as in zinc
so that ignition can take place. Third, three of these metals
have low oxide melting points near or below the metal igni-
tion temperature. This obviously limits the protective qual-
ities of the oxide to that temperature at which melting occurs.

Now, the fact that a particular metal has a thin porous
oxide coating easily explains why the ignition temperatures
for such metals, whether obtained in an induction or resis-
tance furnace, are in excellent agreement. This type of
oxide layer does not prevent the natural diffusion of oxygen
to the surface of the parent metal. Thus, no matter whether
heating is accomplished in an inert or oxidizing atmosphere,
the oxide coat cannot have any influence on the results since
the metal is obviously critical temperature controlled. This
is indeed the case for the aforementioned metals--bismuth,
lead, magnesium, molybdenum, which, as pointed out previously,

show very good agreement between the present results and those of Grosse & Conway. Indeed, other results (12, 37) obtained by heating in an oxygen atmosphere with a resistance furnace, indicate that magnesium has an ignition temperature that is very reproducible under varying environmental conditions.[7]

The correlation between these two sets of ignition temperatures is also very good for zinc. As seen previously, however, zinc is a transition temperature controlled metal with an apparently highly protective oxide shell. Since the ambient inert gas pressure for the Grosse & Conway experiments is one atmosphere, then good correlation may be expected since the very thin, but highly protective oxide layer, formed immediately upon exposure of the zinc metal to the oxygen gas, will protect the zinc metal until the boiling point effect takes control of the ignition process.[8]

One could perhaps argue that this good correlation indicates that the ignition of zinc may be ultimately controlled by the need for a certain amount of metal vapor in the atmosphere before ignition can proceed, and that this amount of vapor can only be attained near the metal boiling point. However, the extensive protective qualities of zinc oxide, as shown by the at times slightly "explosive" action involved in the ignition process, even at only 300 torr, indicates that the former explanation, which also accounts for

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[7]This effect may however be due to the fact that the ignition temperature for magnesium falls very close to the metal melting point.

[8]Also important here may be the natural room temperature oxide coating on the surface of the zinc metal.

the variation in zinc's bulk ignition temperature, is much more probable.

Consider now those metals for which the ignition temperatures from these two experimental investigations are different. These include the metals barium, calcium, iron, strontium, and tin, with the last of these having the smallest difference in data. All of these metals have one thing in common: If heated in an oxidizing atmosphere, their oxides are either protective to a very high temperature, or their oxide layers are so thick that they hinder the ignition process by allowing only a small fraction of the needed oxygen to the metal substrate, thus delaying the actual ignition process of the metal. In addition, some metals, because they are suddenly exposed to an oxygen atmosphere at high sample temperatures, undergo a large amount of self-heating which, if ignition is attained, could easily account for the disagreement in these two investigations. For all of these metals then, the difference in the ignition temperatures between the two sets of data is hypothesized to be due solely to whether an inert or oxidizing atmosphere is used in the metal heating cycle of the ignition process. Obviously, the heating process is of critical importance in determining the ignition temperature since the whole concept of the transition temperature is dependent on the establishment of a protective oxide layer on the bare metal. Thus, for example, the large difference in ignition temperature for iron is clearly very strongly dependent on the fact that the transition temperature for iron is over 1200°C. (Here the oxide coating is thin, but impervious and thus the data in the present investigation are found to be very reproducible.)

On the other hand, metals such as tin and strontium have very thick oxides which could easily interfere in the

ignition process. In the case of strontium, for example, the metal, although melting at 774°C, stays in its original geometrical form in an artificial crucible made of a very thick layer of SrO (metal oxide melting point is equal to 2430°C) until ignition occurs. Moreover, the thermocouple traces for tin, strontium, calcium, and barium indicate that self-heating can occur for these metals at relatively low temperatures, especially for barium and calcium. Therefore, the so-called ignition temperature for these two metals, as measured by Grosse & Conway, may be much closer to the respective critical temperature for the same metal. For example, in the heating of barium, the temperature of the bulk sample tended to quickly increase near 150°C (Grosse & Conway ignition temperature is equal to 175°C) until the heating process was quickly slowed down by the automatic control mode of the induction furnace. If oxygen were suddenly flowed over a barium sample which had little oxide protection, it appears very probable that the sample could easily self-heat to ignition. In other words, in the type of experiments performed by Grosse & Conway, it is not possible to discern between the critical and experimental bulk ignition temperatures for metals such as barium and calcium.

For metals like tin and especially strontium which have very thick oxides which may not adhere to the metal in the same way from run to run, it is possible to have a large variation in the measured ignition temperatures at the same pressure as can be seen in Table 6. Metals like barium which have both a thick oxide and a strong tendency to self-heat can also exhibit a large variation in the measured data. However, the complete results for calcium indicate that the ignition temperatures obtained in the present investigation are very reproducible, although they become less so at higher oxygen pressures, indicating that the growth of the oxide shell does

indeed cause greater variation in the measured data. The reproducibility of the calcium data shows, as can be observed at room temperature, that calcium has a more consistent type of oxide layer covering the metal surface and that these measured ignition temperatures should be considered completely credible.

Mellor (12) also obtained similar ignition temperatures in his study of the ignition of calcium ($T_{ign}=805^{\circ}C$). However, he stated that since Grosse & Conway obtained a value of $550^{\circ}C$ for the ignition temperature of calcium, it seemed impossible to define a consistent bulk ignition temperature for metals, and that the transition temperature, although at times difficult to determine, remained as the only consistent temperature available in dealing with the metal ignition problem.

This conclusion is too restrictive in light of the previous discussion on the consistency between the two sets of experiments, especially for metals like bismuth, lead, magnesium, molybdenum, and zinc. The disagreement between Grosse & Conway and the present investigation may again be explained through the difference between the critical or spontaneous ignition and true ignition temperatures as evidenced by the process of self-heating that was observed in some of the runs with several of these metals. In dealing specifically with bulk calcium (See Table 7), other experiments done in a flowing stream of air by Reynolds (22) also give comparable ignition temperatures over $700^{\circ}C$. Reynolds' results are lower than those of the present investigation perhaps due to the fact that the room temperature oxide scale was removed before the experiment was begun. However, his results are significant since they do indicate a high ignition temperature for calcium heated in an oxidizing atmosphere in a

completely different type of ignition environment. (In addition, Reynolds found that the ignition temperature of calcium was <u>not</u> appreciably influenced by a higher velocity airflow perhaps indicating that either the airflow could not blow the oxide scale off or that the removal of sections of the oxide scale had little effect on the ignition temperature. Although the cooling effect of the airflow could not be discerned, Reynolds' work is more evidence to show that calcium is, in all probability, a critical temperature controlled metal.)

The above results, especially for calcium, along with those of the present experimental work have convinced this investigator that a consistent bulk ignition temperature can be defined for most metals in an oxygen atmosphere over a fairly large range of experimental conditions. In other words, the ignition temperature will depend on, for example, the ambient pressure and the type of oxidizing atmosphere; however, the metal ignition temperature will not strongly depend on the heating environment. Thus, measurements of the ignition temperature in an oxygen atmosphere, whether the sample is resistance or induction heated, would be expected to give comparable results. Consequently, the metal ignition temperature is here postulated to be a much stronger function of the particular metal than of the environment used in the heating process.[9]

3. The Ignition Phenomenon

Contributions to an understanding of the physical process of ignition can be made not only through a tabulation of ignition temperatures, but also through a visual description

[9]Mellor (12) did indeed find a $15^{\circ}C$ change in ignition temperature for calcium at one atm when a resistance-type heating system was used in the induction furnace. This, however, is a small variation compared to that of the ignition temperature between different metals.

of the ignition phenomenon for various metals. This type
of study may conveniently be divided into two classes: (1)
Those metals which undergo vapor-phase combustion; (2) Those
metals which burn on the surface.[10]

a. Metals Which Combust in the Vapor-Phase

The following metals are observed to ignite such that
combustion occurs as a vapor-phase flame: barium, calcium,
magnesium, strontium, zinc. All of the above ignite in a
sudden unexpected and explosive flash of light so strong that
the process must be observed through a neutral density fil-
ter. The entire sample is instantaneously engulfed by flame
and light; there is a vary rapid temperature rise which immed-
iately takes the thermocouple reading off scale. At higher
pressures, the ignition process is, as expected, much more
violent and here the metal is essentially consumed by the
time the pressure vessel has been purged and the flame ex-
tinguished.

The metal, zinc, has already been discussed in quite
some detail; however, some aspects of its visual ignition
process lend support to the conclusions made in Section 1 of
this chapter. The ignition of zinc is usually quite violent;
many times zinc metal is scattered to the walls of the pressure
vessel. This is apparently due to the protective qualities
of the oxide layer on the sample. During the heating pro-
cess, enough oxide builds upon the nascent surface so that
when melting occurs, the oxide is observed to hold up for
a short time and then collapse as one unit over the molten
metal. As heating continues, the oxide coating appears to
swell to some degree. Near the very end of the heating pro-
cess, slight fissures begin to appear along radial lines of
the sample. This process perhaps weakens the oxide shell

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[10]Table 7 is used as a primary source in the following
discussions.

and ignition then occurs in a sudden flash of black smoke followed by the engulfment of the entire sample in a yellow-orange flame.

The other four metals that burn in the vapor phase (Mg, Ca, Sr, Ba) are members of group IIA of the periodic table, the so-called alkaline earth metals. Magnesium grows a very thin oxide coat and its ignition temperature, although measured very often in many different types of experimental environments, seems to have a very consistent value of near $630^{\circ}C$. This temperature is extremely close to the melting point of magnesium, which, acting like a large heat sink, could perhaps explain both the lack of a noticeable amount of self-heating for this metal and the consistency in the data determining its bulk ignition temperature.

The other three alkaline earth metals, barium, calcium, and strontium all have very thick oxide layers, even at room temperature. All are highly susceptable to self-heating at even ordinary room temperatures, especially in the case of barium. The thick growth of oxide on these metals may hinder the ignition process to varying degrees, since ignition will depend to some extent on a partial breaking down of the oxide coating. The critical temperatures for these three metals are all below their respective melting points, but the ignition temperature may rise above the melting point due to a combination of the oxide scale and the unique ability of this group of metals to self-heat to ignition. This ability to self-heat is especially true of barium when heated at higher pressures.

For magnesium, calcium, and strontium, there was much flashing over the metal surface just before ignition took place. This phenomenon may be indicative of the amount of vapor over the specimen for these particular metals. In the case of barium, for example, which is the least volatile of

the alkaline earths (40), no such flashing phenomenon was observed before ignition occurred. In fact, at 300 torr, it appeared that barium was approaching closer to a surface type of combustion process.

b. Metals Which Combust on the Surface

The remaining metals in Table 7 are observed to ignite such that combustion takes place on the surface of the metal specimen. These include bismuth, iron, lead, molybdenum, and tin. For these metals, the ignition process, unlike those metals which ignite such that combustion occurs in the vapor phase, does not immediately cause the entire sample to be en-gulfed in flame; there is no sudden flash of light, although a certain brightness does quickly appear on the surface at ignition indicating that some type of relatively fast burning process leading to the formation of the metal oxide has been initiated on the surface of the metal. Since the reaction takes place on the surface and not immediately throughout the metal volume, the temperature rise rate at ignition of a surface burning metal simply changes slope and becomes much faster. However, there is no large temperature discon-tinuity as in vapor-phase flames because the thermocouple does not respond to the flame temperature, but rather to the internal temperature of the sample which rapidly increases due to the conduction from the surface of the sample where reaction between the metal and the oxidizer gas is proceeding.

Consequently, at low pressures, the ignition of a surface burning metal may be very difficult to pinpoint. Thus tin, because of its thick oxide coat, produces a very dim flame at lower pressures that does not appear to spread over the entire metal surface until some time after the first flame has appeared. In fact, as is the case for all of these

surface burning metals at the 300 torr pressure level, the
reaction that occurs after ignition is not generally self-
sustaining and may be extinguished by letting enough oxide
build up on the surface during the combustion process. At
higher pressures, however, the ignition of tin and other
surface burning metals is very clear, from both the appear-
ance of the flame and the change in slope of the temperature
rise rate as recorded by the sample thermocouple. In
addition, of course, the combustion at these pressures
(1 atm, 5 atm) seems to be entirely self-supporting in al-
most all cases.

The heavy metals, bismuth and lead, also produce very
low flame temperatures at low pressures. Such temperatures
again do not allow the flame to be self-supporting at these
conditions. For both of these metals, there is only a very
thin layer of metal oxide built up on the molten metal before
ignition occurs. Ignition usually occurs at the edge of the
crucible and the flame then travels in almost a perfect
circular geometry to the center of the crucible until the
entire surface is undergoing reaction.

Bismuth is the only metal investigated here which does
not appear to obey the metal combustion criterion outlined
in Chapter I. Because bismuth's oxide boiling point is
greater than its metal boiling point, according to the
criterion, bismuth should undergo vapor-phase combustion.
At all pressures used here, though, bismuth definitely
burned on the surface; however, at 5 atm, the ignition is
very violent and appears to be in a vapor-phase form. But
in a very short time, the reaction appears to move back to
the surface. Thus it may be that bismuth could, like boron,
undergo both types of combustion, depending on the ambient
pressure used in the combustion process.

The last two surface burning metals, iron and molybdenum, give results that are the epitome of consistency in such experiments. As in bismuth and lead, the ignition of iron takes place when a small flame appears at one corner of the sample, perhaps where there is a slight crack in the oxide. The flame then spreads across the entire sample surface, melting away the oxide surrounding it as it does so. The initial ignition, however, may not be due to the melting of the oxide, but to a cracking of the oxide shell by the γ-δ solid phase change for iron which occurs near $1390^{\circ}C$ (41).[11]

The ignition and combustion of molybdenum is probably the most unique and yet the most beautiful to observe among those metals investigated in the present work. The ignition process is very much like the other surface burning metals in that a glow appears at one corner of the sample where the oxide has perhaps cracked and then the reaction quickly covers the entire surface as the oxide melts away. Here, however, the oxide melts away very easily and rapidly thus giving rise to excellent reproducibility in the ignition temperature. As the ignition process occurs, black smoke pours from the surface until the entire sample is free of oxide. The reaction then proceeds rather slowly and fairly close to the surface. The combustion is unique in that a light smoke comes from the surface during the entire combustion process. Yellow needle-like crystals of MoO_3 fly from the surface and float through the atmosphere until they settle back on the sample.

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[11] There are several changes on the surface of iron as it is being heated that may also be some type of phase change. The sample surface darkens considerably near $1075^{\circ}C$ and then lightens again at $1190^{\circ}C$ just before the ignition process begins.

This process tends to cut off the oxygen supply and at lower pressures, the flame may be choked and the reaction slowed down considerably. The molybdenum metal remains solid and disappears rather quickly; the entire burning process appears to be more similar to the ablation of a material rather than to its actual combustion.

In retrospect, the ignition of all of these surface burning metals have one particular thing in common: For each, it visually appears that the oxide coat must be completely melted before the flame can become hot enough so that the reaction may be self-sustaining. This seems to be very important for such metals, which have comparatively low flame temperatures and slow reaction rates. Indeed, a quick look at Table 7 shows that the metals with the five lowest metal oxide melting points are surface burning metals. This fact is indeed appropriate since those metals with the five highest metal oxide melting points would thus tend to have the most stable metal oxides. Therefore the oxide boiling point could then be higher than the metal boiling point, consequently producing a metal that burns in the vapor phase.

It appears then that the flame temperatures produced by surface burning reactions are such that the metal oxide must be removed from the surface before combustion can become self-sustaining. Therefore, the ignition temperature for such metals must be fairly close to the metal oxide melting point. Indeed, the ignition temperatures measured in the present investigation are all within $100^{\circ}C$ or so of the appropriate metal oxide melting temperature. (This is especially true at the lower pressures, as expected). In this case then, there appears to be a direct correlation

between the ignition temperature of a metal and the melting point of the metal oxide. Although the metal oxide melting point does not have to be reached to have ignition, it is important that ignition occur at a high enough temperature to cause some small flame to start the oxide melting process.

4. The Effect of Ambient Pressure

One of the more interesting influencing factors upon ignition is the total pressure of oxidizer used in a single experimental run. For example, in the study of zinc undertaken in the first section of this chapter, it was found that the ambient pressure had a great deal to do with the ignition temperature, since here the boiling point of zinc was so crucial to the ignition process. The case of zinc is probably quite unique in the sense that such a large variation in the ignition temperature might not be expected for most metals.[12] However, large variations in ignition temperature may certainly occur over a large pressure range. For example, titanium is reported to have ignition temperatures of 1300-1600°C in the 15-200 psia range while it has ignition temperatures of 850-1300°C at high pressures in the 200-700 psia range (17).

In this section, an extremely simple qualitative approach to this problem is outlined. The final results seem to show that critical temperature controlled metals have ignition temperatures that decrease with increasing pressure, while metals that are transition temperature controlled may perhaps

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[12]This large variation in the ignition temperature for zinc, by the way, allows for a very good estimation of the critical temperature for this particular metal. That is, for any metal, the lowest value of the experimental ignition temperature places a maximum value on the critical temperature, from which the sample may self-heat to ignition. Therefore, considering the typical values of the experimental ignition tempereatures for zinc (~1000°C), the lowest value of its ignition temperatures (785°C at 200 torr; See Table 5) places an excellent upper limiting value on its critical temperature.

be expected to have ignition temperatures that either increase with increasing ambient pressure or remain relatively constant over a large pressure range.

In order to undertake this problem, it is necessary to consider two cases: (1) A metal whose oxidation rate is protective, i. e., in most cases, parabolic; (2) A metal whose oxidation rate is nonprotective, or linear. If a metal has a protective oxide layer, then an increase in pressure will increase the amount of reaction such that a greater oxide layer will build on the metal substrate per unit time. Thus, when the ignition process begins to develop, there is a thicker, stronger protective oxide layer which must be broken before ignition can take place. Therefore, in this case, the ignition process should be more difficult and higher ignition temperatures would be expected.

On the other hand, if a metal has a non-protective oxide layer, then oxygen is always able to reach the metal substrate. Hence, an increase in pressure here will allow more oxygen to diffuse through the porous oxide layer and thus the reaction rate at the metal surface would be expected to increase. This higher reaction rate then increases the amount of heat produced at the metal surface per unit time. Therefore the critical temperature for the metal-oxidizer system will decrease since the $\dot{q}_{chem}$ curve (See Fig. 3) has shifted to higher values. Thus the ignition temperature for a metal which is not protected from further gas-phase oxidation by a protective oxide layer will tend to decrease with an increase in pressure.

Unfortunately, very few metals undergo oxidation that is purely parabolic or purely linear. The relative amount of oxidation of each type that a particular metal will experience is given by its transition temperature. Thus if a

metal has its transition temperature at or close to the
ignition temperature, the metal undergoes a protective
oxidation rate nearly all the way to ignition. On the
other hand, a metal with a very low transition temperature
has a non-protective oxidation rate law at nearly all
temperatures up to ignition.

It appears then that a critical temperature controlled
metal, for which the transition temperature is fairly low,
as in most cases, will experience a drop in the ignition
temperature with an increase in pressure. Likewise, a
transition temperature controlled metal, for which the
transition temperature is fairly high as in almost all cases,
will experience either an increase in the ignition temper-
ature with pressure or a constant value of the ignition
temperature with any change in pressure, depending on the
process by which the oxide shell is removed. If the oxide
layer is made non-protective via breaking and cracking, then
an increase in ignition temperature is expected with in-
creasing pressure since more mechanical strength will be
needed to break a thicker, stronger oxide coat. Of course,
if the ignition temperature is strongly dependent on the
boiling point for a certain range of pressures as for zinc,
aluminum, and perhaps cadmium, a large increase in ignition
temperature with increasing pressure is also to be expected.
However, if the protective oxide shell can only be removed
via a melting process, then the ignition temperature is
expected to remain relatively constant with variations in
pressure.

For those critical temperature controlled metals which
have a very high transition temperature, and especially for
transition temperature controlled metals which have a
transition temperature somewhat lower than the ignition

temperature, there is no assurance of the exact type of variation of ignition temperature with pressure that might be expected.

The above conclusions seem to be intuitively correct, but it was necessary to show that indeed critical and transition temperature controlled metals could be differentiated by whether their ignition temperature respectively decreased or increased with an increase in the ambient oxygen pressure. Unfortunately, the present investigation does not cover a wide enough range of pressures to show conclusively if the simple arguments used above have complete validity (See Table 6). Neither do any of the results deny the conclusions reached above, but rather they somewhat reinforce them. For example, almost all the metals used here are critical temperature controlled and most of them show a decrease in ignition temperature with pressure. The one definite transition temperature controlled metal, zinc, does show the expected increase in ignition temperature with an increase in pressure. The decrease in ignition temperatures for barium and tin are not as definite, but again do not deny the above conclusions. Strontium appears to be a transition temperature controlled metal based on its ignition temperature variation with pressure. There is no way to prove or disprove this since strontium oxide is visually very thick and protective and yet there is no available oxidation information in the literature which can be used to approximate a transition temperature. Iron offers the only other anomaly here since it may very well be a transition temperature controlled metal, and yet it has the opposite pressure variation.

As for all of these metals, only further investigation over a much wider pressure range can demonstrate conclusively, as it does for titanium (17), the exact type of variation

in ignition temperature that any particular metal may have
with pressure. Furthermore, only such investigations can
show whether or not the type of ignition temperature varia-
tion is dependent on the particular temperature, critical
or transition, which controls the ignition for any one metal.
5. Fragmentary Data on Other Metals

This short section simply outlines the more important
results obtained in fragmentary experiments with five other
metals which were not investigated extensively as were the

TABLE 8

IGNITION TEMPERATURES OF OTHER METALS

Metal	Pressure (atm)	Ign. Temps ($^\circ$C)	Other Results ($^\circ$C)
Cu	1	>1085	>1085 (17,22)
Co	1	>1400	-
Ti	1	>1410	1570-1620 (22), 1315 (42)
W	1	>1375	1240-1290 (22)
	5	≈1230	1240-1290 (22)
Zr	1	~1800	-

metals previously mentioned in this report. These metals in-
clude copper, cobalt, titanium, tungsten, and zirconium.
The latter three were ignited at least once while copper and
cobalt were only heated to the limit of the chromel-alumel
type of thermocouple used in this investigation. Table 8
lists the results of the present investigation along with other
data from the literature. Ref. 17 was used as the major source
of compiled bulk ignition temperatures for these metals.
Most of the data listed in Ref. 17 were taken from the work
of Reynolds (22) in which static ignition tests were done in

atmospheres of air from pressures of 1 to 7 atm.

The three metals which ignited (Ti, W, Zr) seemed to burn on the surface. Tungsten did not ignite at 1 atm, but did ignite at 5 atm near 1230°C, and thus is in good agreement with the results of Reynolds. Titanium ignited shortly after the thermocouple broke at 1410°C. If the ignition temperature of Ti is estimated at near 1500°C, then the results of Reynolds (22) in _air_ are too high while those of Dean and Thompson (42) in oxygen, but at 3.3 atm, are too low. Obviously, more definite work must be undertaken in this case. Zirconium also burned on the surface, but it did not visually begin to react until long after the thermocouple became useless. However, its ignition temperature was estimated at 1800°C since reaction appeared to begin just before the metal started to melt.

The above three metals (See Table 4) all have very high metal oxide melting points and fairly low transition temperatures relative to these melting points. In such cases then, as shown by the estimated ignition temperatures for these metals, it does not seem necessary, as it appeared to be for the other five surface burning metals investigated here, that the oxide coat melt before surface reaction can continue. This may be true because the oxide coating becomes non-protective at temperatures significantly lower than the metal oxide melting point.

Some sections of the cobalt sample seemed to melt but a very strong oxide coat remained on the sample. Indeed cobalt has a very high transition temperature (> 1350°C) and some of its alloys have been reported not to ignite until they melt (17).

Copper definitely did not ignite at least until after it melted. After melting, the molten metal underwent vigorous

motion in its crucible and got significantly brighter. In addition, the molten copper then destroyed the crucible and thus the experiment had to be ended. Because the metal became so bright at temperatures measured as high as 1250°C, surface ignition could not be discerned; in addition the vigorous motion of the molten copper and the disintegration of the Al_2O_3 crucible disrupted the thermocouple readings such that a change in slope in the rate of temperature rise was impossible to determine. The appearance of CuO on the metal surface after the run is indicative of reaction, but this may also be the product of a vigorous oxidation process.

6. Metal Ignition: A Complex, Unsolved Problem

Although much has been accomplished in the field of metal combustion in the last decade, there still remains much to be done. Even less understood is the ignition of metals. Of all the concepts discussed in the present report, perhaps none will be used in future developments as much as the simple experimental ignition temperatures obtained for the ten metals of prime interest, as discussed in Section 2 of this chapter. If the bulk ignition temperature is truly consistent for most metals, irregardless of the type of heating environment used in any experimental situation, then perhaps the present data can serve as a starting point for an extended experimental and theoretical study of this difficult problem.

Experiments similar to that of Grosse & Conway may be used to determine the critical temperatures of metals. Once these are known, a study of the mechanism of self-heating and the phenomenon of pyrophoricity can be undertaken. When these experimental problems are at least in some way better

understood, then theoretical work may be able to better explain and define the ignition process.[13]

This developmental procedure must stress the need for a more quantitative approach to the problem of the heterogeneous ignition of metals. Not only can this approach lead to a better understanding of the surface phenomena, such as gas phase chemisorption, oxidizer diffusion, and metal oxidation, that lead to ignition, but also, some of the important defining temperatures used in the present model may perhaps be correlated, at least for metals in oxygen atmospheres. A theoretical microscopic approach to this problem might then be able to predict critical or ignition temperatures for various metals; such a theoretical model must however, relate surface oxidation to ignition and ignition to combustion, whether surface or vapor phase. Note here, also, that the prediction and correlation of ignition temperatures, whether bulk or spontaneous, will in all probability depend on many factors; there does not appear to be any method to correlate such temperatures to some function of a simple property of metals as suggested by Grosse & Conway (38).[14]

In theoretical studies of self-heating and pyrophoricity, it might prove necessary to use a non-steady approach to the problem. This is due to several reasons: (1) Oxidation may be parabolic or linear. (2) Self-heating to ignition takes

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[13] This is the third mode of development outlined in Chapter III.

[14] In many attempts to correlate the self-heating characteristics of the alkaline earth metals to their heat loss characteristics, however, it was found that increasing capacity to self-heat correlated well with decreasing values of specific heat, c_p. Unfortunately, attempts to further substantiate this by correlation with the thermal diffusivity could not be undertaken because of lack of data for these metals on the thermal conductivity, $k_{cond,f}$.

place in a wide range of times for different metals.   (3) Self-heating depends on sample size.   (4) Pyrophoricity depends on sample size and on the time necessary to conduct heat from the sample surface to the sample volume.

In conclusion then, all of the theoretical and experimental work that must be done to better understand the meaning of the critical temperature, self-heating, and pyrophoricity will hopefully lead to a significant improvement in our knowledge of metal ignition. This knowledge will someday be applied in order, for example, to augment metal ignition by coating hard to ignite metals like aluminum with easy to ignite metals like magnesium such that the ignition and combustion of magnesium will lead to the combustion of the aluminum substrate. These types of improvements can be used to greatly increase the efficiency of modern rockets and to develop future "air" breathing engines that can supply useful power on other planets.

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